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(LITE)

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I. INTRODUCTION

Light emitted from high temperature black smokers (350°C) at mid-ocean ridge spreading centers has been documented (Van Dover et al. 1988), but the source of this light and its photochemical and biological consequences have yet to be investigated. Preliminary studies indicate that thermal radiation alone might account for the "glow" (Smith & Delaney 1989) and that a novel photoreceptor in shrimp colonizing black smoker chimneys may detect this "glow" (Van Dover et al. 1989; Pelli and Chamberlain 1989). A more controversial question is whether there may be sufficient photon flux of appropriate wavelengths to support geothermally-driven photosynthesis (GDP) by microorganisms (Van Dover, Cann, Delaney, unpublished).

Although only a very low level of visible and near-infrared light may be emitted from any single hydrothermal vent, several aspects of the light make it of more than enigmatic interest: First, the light is clearly linked to geophysical (and perhaps geochemical) processes; its attributes may serve as powerful index parameters for monitoring change in these processes. Second, while the glow at a vent orifice is a very local phenomenon, more expansive subsurface environments may be illuminated, thereby increasing the spatial scale at which biological consequences of this light might be considered. Third, in contrast to intermittent bioluminescent light sources in the deep-sea, the light emitted at vents almost certainly glows or flickers continuously over the life of the individual black smoker (years to decades); collectively, light emitted from black smokers along the ocean's spreading centers superimposed on background Čerenkov radiation negates the concept of the deep sea as an environment devoid of abiotic light. Finally, the history of hydrothermal activity predates the origin of life; light in the deep sea has been a continuous phenomenon on a geological time scale and may have served either as a seed or refugium for the evolution of biological photochemical reactions or adaptations.

II. EXECUTIVE SUMMARY

The idea that deep-sea hydrothermal vent environments might be a non-solar photic habitat arose from observations of a novel photoreceptor in shrimp (*Rimicaris exoculata*) that dominate Mid-Atlantic Ridge hydrothermal vents. Attributes of this photoreceptor -- its large size, lack of image-forming optics, high pigment concentration, and reflectivity -- all support the hypothesis that the photoreceptor is adapted for detection of a very dim source of light. Ambient light conditions of shrimp-dominated vent environments have yet to be explored. But, reasoning that one source of dim light specific to all high-temperature vent environments is thermal radiation of 350°C+ fluids, a successful effort to document ambient light at black smokers on the Juan de Fuca Ridge was made using a commercially available CCD (charge-coupled device) camera. The images obtained from 10-sec exposures of a non-artificially-illuminated 350°C vent showed an eerie glow most intense at the orifice and diminishing to below detection at distances 20-30 cm above the exit.

The *LITE Workshop*, held at the Woods Hole Oceanographic Institution in Woods Hole, Massachusetts on 10-12 January 1993, was convened to reexamine the interpretation of plausible sources of the glow and the nature of the general photic environment of deep-sea hydrothermal vents. Participants were also asked to consider the potential photobiochemical consequences of the glow. The workshop was international and interdisciplinary in scope, with experts from the US, UK, France, Germany, Russia, Norway and Sweden representing fields of geophysics, physical chemistry, geochemistry, astrophysics, instrumentation, CCD technology, microbiology, photosynthetic energetics, photosynthetic pigments, vent ecology and sensory physiology. The workshop was sponsored by NSF, NASA, and the NSF-RIDGE Office.

Plenary sessions of the workshop were interspersed with Working Group Sessions charged with three tasks:

i) characterization of observed light, identification of plausible sources of this light and prioritization of instrumentation and observations required to characterize ambient light conditions at vents more completely;

ii) evaluation of the potential for geothermally-driven photosynthesis;

iii) identification of issues in sensory biology of photoreceptors in vent organisms.

A consensus was reached among all participants that quantitative spectral characterization of ambient light conditions at hydrothermal vents is one of the highest research priorities. Determination of fundamental optical properties of vent water -- including transmission, emissivity, and refractive index -- is essential. Recalculation of photon fluxes by workshop participants confirmed that thermal radiation is a plausible source of light at high temperature vents, but other sources of light, notably crystalloluminescence, might be superimposed on the thermal radiation spectrum. Comparison of spectral properties of light emitted by turbulent jets and standing pools of high temperature water were cited as valuable in understanding the photic diversity of vent systems. Phase-separated fluids and supercritical fluid conditions provide other natural variations on the photic potential of vents, ones that participants believed should be explored both in the laboratory and in the field. An effort should also be made to evaluate the role that enhanced bioluminescence within vent fields might play in generating a light stimulus important in the sensory biology of shrimp. Investigation of the optical properties of vent water and the spectral quality of the ambient photic environment at vents requires development of specific instrumentation to undertake *in situ* observations.

Participants critically evaluating the potential for geothermally-driven photosynthesis found themselves working at the edge of the envelope. Minimum photon requirements for the existence of phototrophic bacteria were calculated to be met within 5 cm of the source of the glow imaged at the Juan de Fuca site. Uncertainties associated with the calculations and the potential for site-to-site variation in light intensity caused by variation in thermal, chemical and physical regimes contribute to the critical need for more thorough field measurements of ambient light conditions. No workshop participant expects phototrophs to be ecologically important at vents, but if phototrophs should exist in the photon-starved environment of vents, they are likely to exhibit properties of interest to microbial biologists. A systematic search for phototrophs was deemed premature until photic conditions are better defined, but opportunistic samples of suitable habitats could be assayed for pigments diagnostic of phototrophic microorganisms.

While sensory biologists concurred with the need for an empirical description of available light in the vent environment, they emphasized that progress in understanding photoreception in vent organisms, specifically shrimp, can be advanced by a series of anatomical, physiological and behavioral observations. The anatomical research agenda emphasizes ontogenetic and comparative studies of eyes in species belonging to the shrimp family Bresiliidae, which exhibit a range of eye morphs from the more normal eyes of *Alvinocaris lusca* to intermediate derivations of *Chorocaris chacei* to the extreme modification exhibited by *Rimicaris exoculata*. Physiological, biochemical and behavioral studies should address the apparent mismatch between the available light and the absorption characteristics of the pigment in the *Rimicaris exoculata* eye.

III. BACKGROUND

[Note: Each workshop participant received this "Background" information prior to the workshop.]

Hydrothermal vent fields are complex hot spring areas found along the crests of mid-ocean ridges (Figure 1). Oceanic crust is typically exposed at these ridge crests and is generated by basalt magma rising from the Earth's mantle as the tectonic plates spread apart. The rising magma collects in magma chambers 1-3 km below the seafloor, underlying segments of the ridge crest. Lava erupts at the seafloor through narrow, dyke-forming vertical fissures. Newly-formed crust is stretched and fractured by the movement of the plates, giving rise to faults that penetrate the upper crust. Seawater percolates down into the new hot crust where it becomes heated and reacts chemically with the rock to be transformed into a hot (350-400°C), acid (pH about 4), sulfide-rich and metal-rich hydrothermal solution. Because the hot solution is buoyant, it rises through the overlying rock. Where the flow is focused, it emerges at the ocean floor to produce the hydrothermal vent fields.

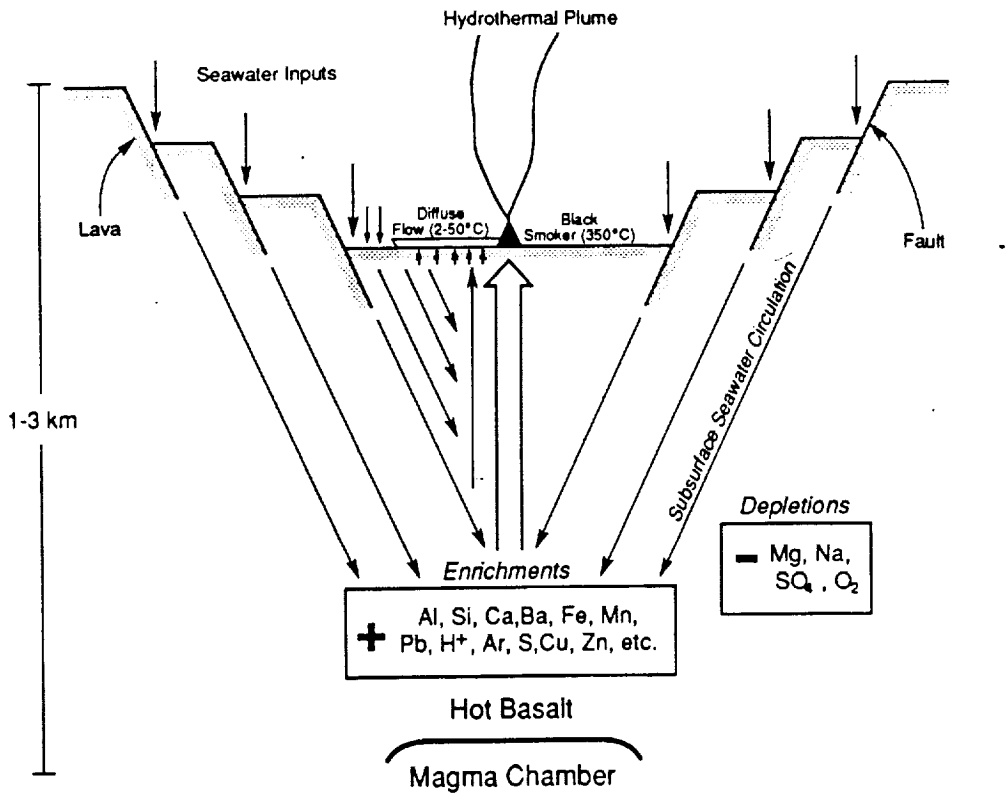


Figure 1. Formation of hydrothermal vents on the seafloor takes place at seafloor spreading centers. Cracks, faults, and other natural permeabilities allow seawater to penetrate the seafloor and react with hot basalt at depth. The chemically modified water rises up to the seafloor to exit as hydrothermal vents. Typical trends in enrichments and depletions of vent water are identified here. From Van Dover 1990.

Relatively uniform geochemistry of the two reactants -- seawater and basalt -- allows for similarity in the major element chemistry of venting waters on a global scale (Table 1). Variability does exist, however, especially in the sulfide/metal ratio, so that some waters are sulfide-dominated and others are metal-dominated. When hydrothermal activity occurs in areas with a high sedimentation rate, the rising fluids can react with sediment trapped between lava flows to produce more variable geochemistry, and even distill hydrocarbons out of the sedimentary organic matter.

Table 1. End-member fluid values for the TAG and MARK vents on the Mid-Atlantic Ridge compared to the OBS vent at 21°N on the East Pacific Rise and seawater. From Campbell et al. (1988) and von Damm et al. (1985).

	TAG	MARK-1	MARK-2	EPR (21 N)	SEAWATER
Temperature (C)	321-290	350	335	350	2
*p*H		3.9	3.7	3.4	7.8
Alkalinity (μmol dm^{-3})		-64	-243	-400	2300
$Si(OH)_4$ (mmol kg^{-1})	22.0	18.2	18.3	17.5	
H_2S (mmol kg^{-1})		5.9	5.9	7.3	
Cl (mmol kg^{-1})	659	559	559	489	541
Na (mmol kg^{-1})	584	510	509	432	464
Li (μmol kg^{-1})	411	843	849	926	26
K (mmol kg^{-1})	17.0	23.6	23.9	23.5	9.8
Rb (μmol kg^{-1})	10	10.5	10.8	23.5	1.3
Cs (nmol kg^{-1})	100	177	181	202	
Be (nmol kg^{-1})		38.5	38.0	15	0.02
Mg (mmol kg^{-1})	0	0	0	0	52.7
Ca (mmol kg^{-1})	26.0	9.9	10.5	15.6	10.2
Sr (μmol kg^{-1})	99	50	51	80	87
Mn (μmol kg^{-1})	1000	491	493	1024	<0.001
Fe (μmol kg^{-1})	1640	2180	1832	1530	<0.001
Cu (μmol kg^{-1})		17	10	35	0.007
Zn (μmol kg^{-1})		50	47	106	0.01
Al (μmol kg^{-1})		5.3	5	5.2	0.005
B (μmol kg^{-1})		518	530	500	

A hydrothermal field is typically 100-200 m in breadth, and contains individual vents of many different kinds (see reviews by Van Dover 1990; Tunnicliffe 1991 for detailed descriptions of vent environments). Some are the classic black smokers, where hot, undiluted fluid is channelized through chimneys of iron, copper, and zinc sulfides. The chimneys vary in size and morphology from site to site. Hydrothermal fluid exits a chimney orifice as a turbulent jet of clear water that within centimeters becomes black with suspended precipitates of metal sulfides -- hence the term "black smokers". The precipitation occurs as the pH is raised and the solution is cooled on mixing with ambient seawater. Horizontal temperature gradients at the vent orifice are extreme, the temperature rising from the ambient 2°C to more than 350°C across a distance of 1-2 mm. Plumes of black smoke can be traced 100-200 m above the seafloor (Baker et al. 1985). White smokers are cooler vents through which water emerges that has been diluted below the seafloor and has lost most of its sulfides by precipitation before exiting. Coolest is the shimmering diffuse flow, which exits over a range of temperature, from 2°C to more than 100°C.

Individual high temperature, black smoker vents emit about 1 kg s^{-1} of hot water. Whole vent fields emit the equivalent of several hundred kg s^{-1} of hot fluid, much of it substantially diluted. This corresponds to a thermal energy flux of about 1000 megawatts.

Direct evidence exists for hydrothermal activity on seafloor spreading centers since the Paleozoic (e.g., Moore et al. 1986), but the lifetime of individual vents and, perhaps, vent fields is more ephemeral. On fast-spreading ridge segments such as the East Pacific Rise, vent fields persist for periods on the order of decades (Macdonald et al 1980; Lalou et al. 1984; Converse et al. 1984). On any given segment, however, expiration of one vent field may be paralleled by the creation of another. At slow spreading centers, such as the Mid-Atlantic Ridge, a single vent field may persist for tens of thousands of years, with active venting intermittent over shorter periods (Lalou et al. 1990; Rona et al. 1991).

Hydrothermal activity associated with submarine volcanism can support life in the absence of sunlight. The chemosynthetic basis for life at vents is found in free-living bacteria that colonize surfaces and hydrothermal fluids and in animal-bacterial symbioses that crowd around diluted hydrothermal effluents (see reviews of Jannasch & Mottl 1985; Karl 1990). In sulfide-dominated vent fields, the warm, dilute vent water contains up to hundreds of micromoles of sulfide, as well as dissolved oxygen from the admixed seawater. It is from such waters that the biological communities of vent fields draw their energy, as bacteria oxidize the sulfide with the dissolved oxygen. Other redox pairs also contribute to the biologically available energy flux. Chemosynthetic primary production by free-living and symbiotic bacteria supports complex food webs with multiple trophic levels and numerous species of invertebrate grazers, suspension feeders, carnivores and scavengers. Compared to terrestrial and shallow-water habitats, deep-sea hydrothermal vents are unique environments characterized by their local insularity, global distribution, individual ephemerality, collective geological longevity, and their physical and energetic isolation from the catastrophic events implicated in the extinction and speciation of terrestrial and shallow-water forms.

In 1989, a novel photoreceptor was described in a shrimp that colonizes high temperature (350°C) black smokers on the Mid-Atlantic Ridge (Van Dover et al. 1989). The authors interpreted the morphology and biochemistry of the eyes as well-adapted for detection of low-level illumination and proposed that they may have evolved as a means of detecting light emitted by black smokers. Planck's Equation defines the total radiant exitance from a perfect blackbody as a function of temperature. In a general sense, Planck's Equation must apply to high temperature (350 to 400°C) plumes of water emitted from black smoker chimneys on the seafloor and to high-temperature seawater circulating beneath the ocean's crust. While thermal radiation from a 350°C body will peak somewhere in the far infrared, the tail of the thermal spectrum will extend into the visible region, where light can penetrate through water and be of potential use in biological systems. Pelli and Chamberlain (1989) calculate that there is sufficient photon flux for the shrimp to see the hot water; at 350°C, the scotopic luminance of vent water is just below the limit of detection by man.

An image of light emitted at deep-sea hydrothermal vents (Figure 2) was obtained using a CCD (Charge Couple Device) camera during an Alvin dive series on the Endeavour Segment of the Juan de Fuca Ridge (47°57'N; 2200 m) in the northeastern Pacific Ocean (Van Dover et al. 1988; Smith and Delaney 1989). A description of the site may be found in Delaney et al. (1992). Photon-to-electron conversion in the camera (quantum efficiency, η) is wavelength-dependent and is maximal at 650 nm (40%) and is >5% for $\lambda < 400$ nm and for $\lambda > 950$ nm. The camera was stably positioned 45 cm from the orifice of a black smoker chimney; water temperature 3 cm within the throat of the smoker measured 356°C. Images were collected with all external lights of the submarine extinguished and with portholes blacked-out. CCD images collected under ambient light conditions show an irregular but sharply-defined line of light that follows the sulfide/jet interface, with the light extending upward into the plume, eventually becoming unevenly dimmer. The same phenomenon was observed at two active chimneys 50 m apart. The light was not detectable by non-dark-adapted eyes. The images suggest that light intensity is correlated with temperature and percentage of hydrothermal fluid. The brightest group of pixels in a series of 10 sec exposures of the same plume consistently gave a measured photon flux of 80 ± 10 photons $pixel^{-1}$ s^{-1}.

Calculated flux of photons (details of the calculations are provided in Appendix 1) from an ideal black body radiator, as detected by the CCD camera (accounting for sensitivity and deployment characteristics

of the camera and absorption of light by seawater along the 45 cm path), is strongly temperature dependent: theoretically, 350°C vent water yields 80 photons pixel^{-1} s^{-1}; 300°C water yields 7 photons pixel^{-1} s^{-1}. These theoretical calculations, assuming an emissivity of 0.25, compare well with the observed brightest flux, suggesting that thermal radiation might provide the major component of the light observed. During a subsequent field study, the site was revisited with the identical camera and collected images through a series of color filters and reflective mirrors. Little effect was detected when color filters were deployed, but an estimated 90% of the image was lost when a mirror reflecting wavelengths greater than 750 nm was placed in front of the camera. This observation is consistent with the hypothesis that the light source is long-wavelength, thermal radiation.

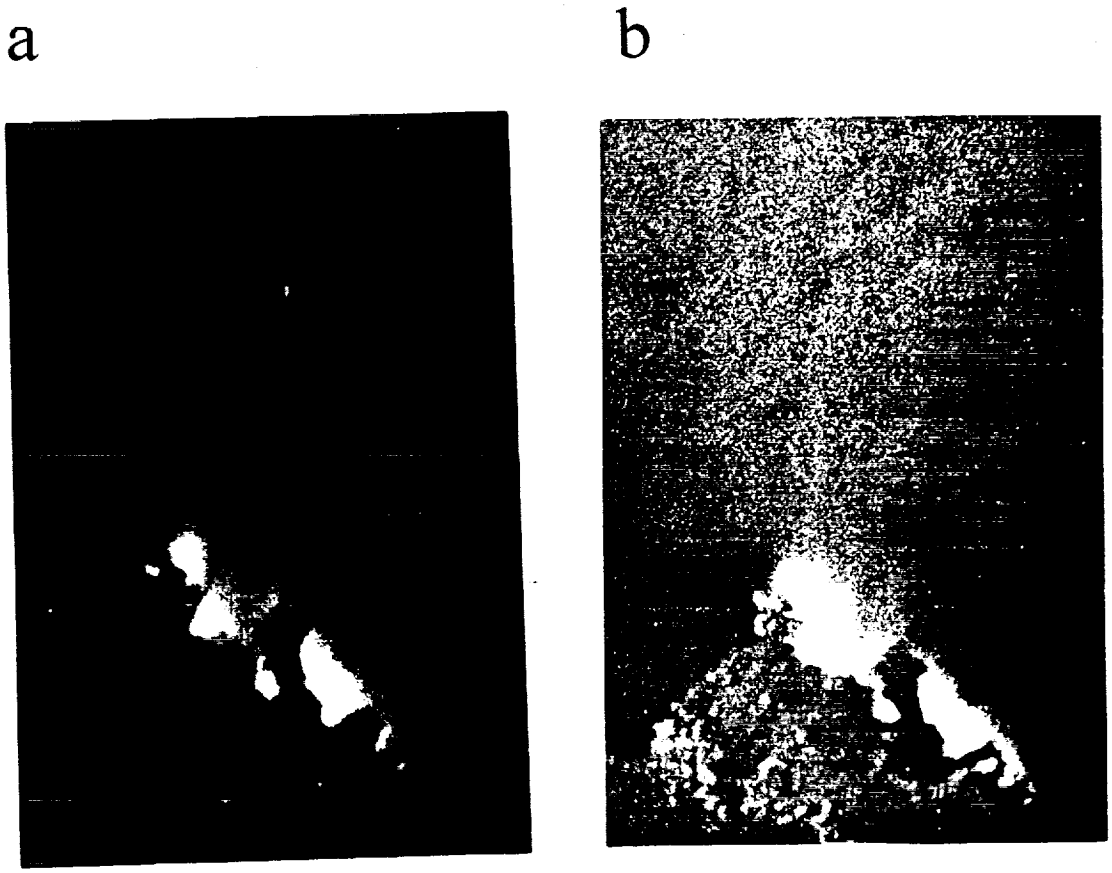


Figure 2. a) Ambient light emitted by a black smoker plume on the Juan de Fuca Ridge. b) Ambient plus reflected light of the same black smoker plume. This image places the vent glow in its physical context. Diameter of the vent orifice is ~ 9 cm. Photos by Smith/Delaney/Van Dover/Cann/Foster, unpublished.

While thermal radiation undoubtedly is emitted from high temperature hydrothermal fluids, other potential, narrow-band sources of light may be superimposed on the blackbody radiation spectrum, including delayed thermoluminescence of metal sulfides, chemiluminescence, cavitation, and Cherenkov radiation. The optical properties of hydrothermal fluids have been virtually unexplored. Given the complex physico-chemical environment of hydrothermal systems, empirical observations may provide the most direct information regarding additional sources of light production at deep-sea hydrothermal vents. The images obtained by the CCD camera provide only an estimate of the spectral characteristics of the glow based on approximate assumptions. Direct spectrophotometric measurements of the light in the regions of interest (visible and near infrared) must be conducted before we can understand the phenomenon and its consequences.

The existence of a relatively steady source of light at depths below the euphotic zone raises the possibility of novel exploitation of that light by biological systems. We know that two caridean shrimp endemic to vent environments, *Rimicaris exoculata* and *Chorocaris chacei*, both have massed photoreceptor arrays backed by biological mirrors. In the black smoker environment, these specialized organs could serve to detect the hot chimney vents and to prevent shrimp from swimming into thermally lethal water. One puzzle is the apparent mismatch between the green-sensitive photopigment in the eyes (though the absorption spectrum of the shrimp visual pigment was only measured to 800 nm) and the predominance of longer wavelengths associated with thermal radiation from black smoker vents (but see Pelli and Chamberlain, 1989).

A still more controversial hypothesis is the possibility of geothermally-driven photosynthesis. Is the photon flux from hydrothermal fluids adequate for photosynthesis by organisms having a photosynthetic pigment that absorbs maximally in the near infrared (e.g., bacteriochlorophyll *b*; Thornber et al. 1978)? A photon flux at 0.0005% of sunlight (9×10^{15} photons m^{-2} s^{-1}) is a threshold requirement for energetically-feasible photosynthesis by macroalgae (Littler et al. 1985). Phototrophic bacteria able to form massive blooms at the chemocline of the Black Sea (about 80 m below surface) have been isolated (*Chlorobium phaeobacteroides*) and estimated to grow at short wavelengths (around 460 nm) of light, with a light flux of about 1.5×10^{17} photons m^{-2} s^{-1}(Overmann et al. 1992). Bacteriochlorophyll *b* with an absorption maximum centered around 1000 nm and positioned 5 cm from a 350°C source of black body radiation (in pure water) would encounter a photon flux of about 2.5×10^{15} photons m^{-2} s^{-1}. Shifting the absorption peak further into the infrared, increasing the temperature of the water, and decreasing the distance between the source of the radiation and the pigment would all increase the photon flux encountered by the pigment. Thus, it is not inconceivable that the energetic requirements for geothermally-driven photosynthesis by organisms similar to purple photosynthetic bacteria with a bacteriochlorophyll-like pigment may be met at high temperature vents.

Phototrophic growth of purple bacteria requires light of a suitable wavelength, anaerobic conditions and either inorganic electron donors (sulfide, thiosulfate, hydrogen) or organic electron donors (fatty acids, dicarboxylic acids and others). Some purple sulfur bacteria are metabolically highly specialized; others are very versatile, growing with reduced sulfur compounds or with organic electron donors either in the light or (micro)aerobically in the dark. At least one thermophilic purple photosynthetic bacterium (*Chromatium tepidum*) has been isolated from a Yellowstone hot spring, with an optimal growth temperature of about 50°C (Madigan 1984, 1986). These environmental conditions are fairly specific; within the vent environment, they may be met within the matrix of sulfide chimneys where strong gradients of temperature and chemistry exist over distances of centimeters and less. If photosynthetic bacteria are to be found, we expect that they will occupy a cryptic niche, perhaps comprising a very narrow band, but one which might extend into subcrustal, sulfide-lined hydrothermal conduits.

One of the most likely habitats that fulfills the requirements of purple photosynthetic bacteria is the recently described sulfide flanges on the Endeavour Segment of the Juan de Fuca Ridge. Standing pools of 350°C hydrothermal fluids are trapped beneath lateral outgrowths of massive hydrothermal mounds (Delaney et al. 1988, 1992). The trapped fluids advect slowly upward through the porous flange material, generating

vertically stratified microenvironments for mineral precipitation and microbiological growth (Goldfarb and Delaney 1989). Diverse physiological groups of thermophilic bacteria are supported (Baross et al. 1989), including dense populations of archaebacteria (Hedrick et al. 1992). Flanges range in size from less than a meter to more than five meters at their widest point and can be thicker than 1 meter at their point of attachment, tapering to a relatively thin (1 cm or less in the extreme case) edge or tip (Delaney et al. 1988, 1992).

If photosynthetic bacteria are found at deep-sea hydrothermal vents, their attributes may provide insight into the diversity and evolution of photosynthetic strategies adopted by microorganisms. The idea that life may have originated, then evolved and dispersed to favorable refuges at deep-sea hydrothermal vents between periods of asteroid impacts and vaporization of shallow-water habitats (Sleep 1991, Baross 1991) raises the possibility that extant vent phototrophs may represent functional types no longer present or severely restricted in shallow-water systems.

Hydrothermal vents are thought to be analogs of primitive environments where the early evolution of life may have taken place. They appear to have served as refuges for microorganisms belonging to ancient lineages. Determination of the quantity and quality of photon flux under theoretical and *in situ* conditions will allow us to evaluate alternative hypotheses regarding the source(s) of the radiation and its suitability as an energy source for descendants of early photosynthetic microorganisms. If phototrophic microorganisms are discovered, their attributes may allow us to re-evaluate current notions of the origin of photosynthesis.

IV. WORKING GROUP REPORTS

A. PHYSICAL PROPERTIES

A.1a Existing Observations of Light at Vents

Preliminary observations (Van Dover et al. 1988, Delaney and Smith, 1989) of light emitted from vents provide constraints on the mechanism of emission and the usefulness of this light for photosynthesis and visible-band navigation for vent shrimp. These observations were taken with a charge-coupled device (CCD) camera external to Alvin through color filters which were sequentially inserted in front of the camera. Based on the attributes of the camera system and the absorption of light in seawater, the calculated flux of photons detected approximately 50 cm away from the vent is approximately 1.2×10^{9} photons m^{-2} s^{-1} at 400-750 nm ("visible" wavelength band) and about 1×10^{10} photons m^{-2} s^{-1} at the far red wavelength band of 750-850 nm. This calculated light flux, particularly in the extreme red and near infrared, increases by several orders of magnitude as one moves to within centimeters of the vent. A few centimeters away from the vent, the photon flux at 990-1060 nm expected from just the blackbody hot water (assuming an emissivity of 0.3) is about 2.5×10^{15} photons m^{-2} s^{-1}. (A more detailed discussion of these calculations is given in Appendix I).

While necessarily crude, these first direct observations of the vent light appear to be roughly consistent with the light flux expected from 620°K black body emission (Figure 3) from the hot turbulent vent water, together with the data on absorption of sea water at various wavelengths (e.g. Smith and Baker 1981, Curcio and Petty 1951). There is agreement within 2 orders of magnitude between these preliminary observations and both the predicted visible/red ratio and the absolute flux. Uncertainties in the emissivity characteristics of the hot water and of the spectral absorption of seawater in the vent environment place large uncertainties on these calculations. There is at present no proof that blackbody radiation is necessarily the sole source of the documented glow. We can state only that blackbody radiation is plausibly the source of some significant fraction of the photon flux. In this report, we will identify other sources of light that might be superimposed on the thermal radiation spectrum (Section A.1c) and specific instruments and experiments that can determine the nature of the light emitted from deep-sea hydrothermal vents (Section A.2). But first we will discuss some of the gaps in our knowledge of fundamental optical properties of vent water that became apparent during the workshop and which are critical to interpretation of ambient light conditions at vents.

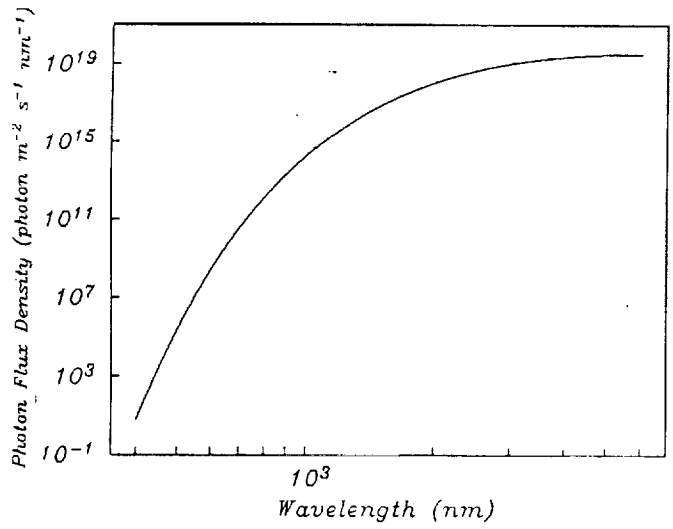


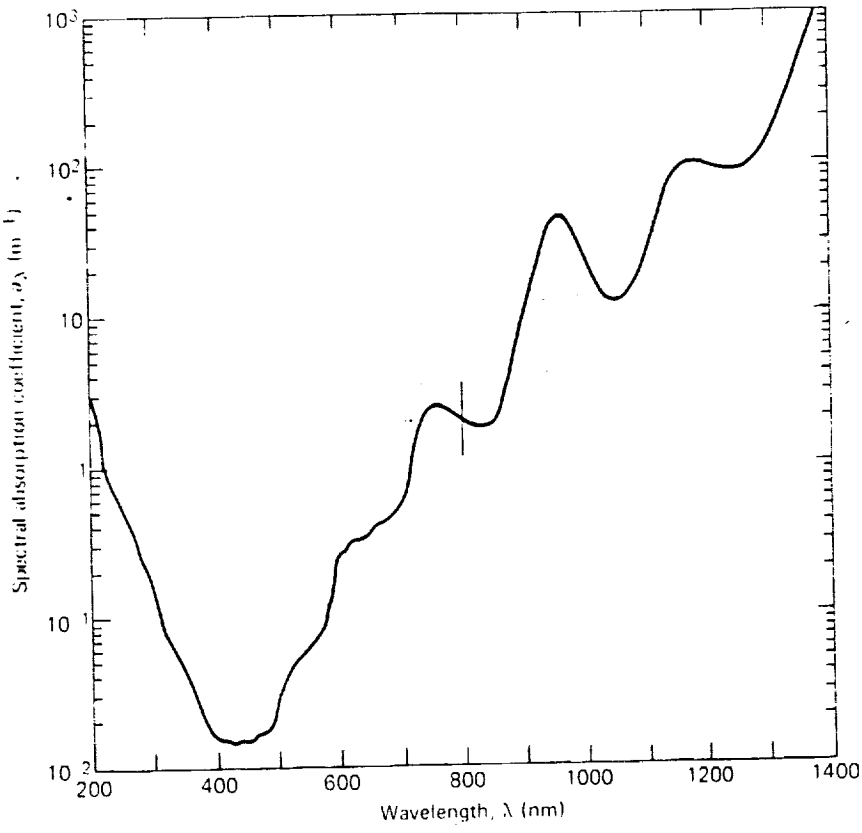
Figure 3. Blackbody radiation spectrum for a 350°C source calculated using Planck's Formula.

A.1b Optical Properties of *In Situ* Seawater and Hydrothermal Fluids

Optical Properties of Seawater at High Temperatures and Pressures

The optical properties of seawater -- *viz.* transmission, emissivity, and refractive index -- at the temperatures (up to 400°C) and pressures (several hundred bars) characteristic of hydrothermal vents, need to be better determined than they are at present. Attenuation of visible and near-IR radiation by seawater between sources and sensors in the vent environment is not sufficiently characterized, although absorption spectra for the clearest waters (Figure 4) can be found (e.g. Smith and Baker 1981, Curcio and Petty 1951). Empirical variations in absorption spectra are presumed to derive from impurities in the seawater. Losses due to scattering (turbidity) in the optical path are not well known. Given the dissolved and particulate impurities of seawater in vent environments, it becomes imperative to conduct fundamental measurements of light transmission *in situ* in order to obtain wavelength-dependent transmission characteristics to account for path-length effects between the source and detector in interpreting experimental observations.

All hot bodies emit thermal radiation, and black smokers are no exception. The intensity of the radiation observed at some distance from a hot body depends on a) how efficiently the radiation is emitted from the body relative to ideal black body emission, (i.e., the emissivity) and b) how much radiation is absorbed between the body and the observer, which depends on the distance and the transmissivity of the medium through which the radiation travels.



Emissivity is inversely related to transmissivity. An ideal black body radiator is, as the name suggests, opaque to the radiation concerned. Transparent bodies, such as hot glass, emit only a small fraction of the ideal black body radiation. A useful concept here is absorbance length -- the thickness of material over

which the intensity of radiation drops by a factor of e. To emit radiation at close to black body intensity, a body must be several absorbance lengths thick. A black smoker 10 cm wide would thus emit efficiently at wavelengths around 1200 nm, where the absorbance length is about 1 cm, but poorly at 600 nm, where the absorbance length is much greater than 10 cm.

Because the black smoker fluids are composed of seawater (albeit chemically modified) and are observed through seawater, there is a strong interaction between emissivity and absorbance length. Though radiation is emitted very efficiently at 1200 nm, its intensity will drop very rapidly with distance from the black smoker, suffering a decrease of more than an order of magnitude over 3 cm. Conversely, radiation of 600 nm wavelength would travel longer distances through the surrounding medium, but will be emitted with very low efficiency. Such a combination of effects limits the intensity of thermal radiation from black smokers and means that the spectrum of thermal radiation will change with distance from the vent.

Two phenomena can allow thermal radiation to penetrate further from a black smoker:

(a) Changes in absorbance of water as a function of temperature. If absorbance increases generally with temperature, then hot water can emit radiation efficiently while cool water remains relatively transparent. Similarly, if the position of absorption bands changes with temperature, then for some parts of the spectrum there would be enhanced emission and reduced absorption. The most recent measurement of absorption of near-IR (750-850 nm) bands of water at temperatures between 0 and 90°C (Collins 1925) shows a significant intensity change and peak wavelength shift for these bands with increasing temperature (Figure 5). Measurements of the Raman band of the water fundamental up to 400°C and 3 kbar pressure (Kohl et al. 1991) suggest that these changes are much more pronounced at the higher temperatures, but these data do not appear to be available for the near-IR bands of interest here. These data are needed for theoretical calculation of the emissivity of the vent fluids, which will affect the total light emission from the presumed black-body source.

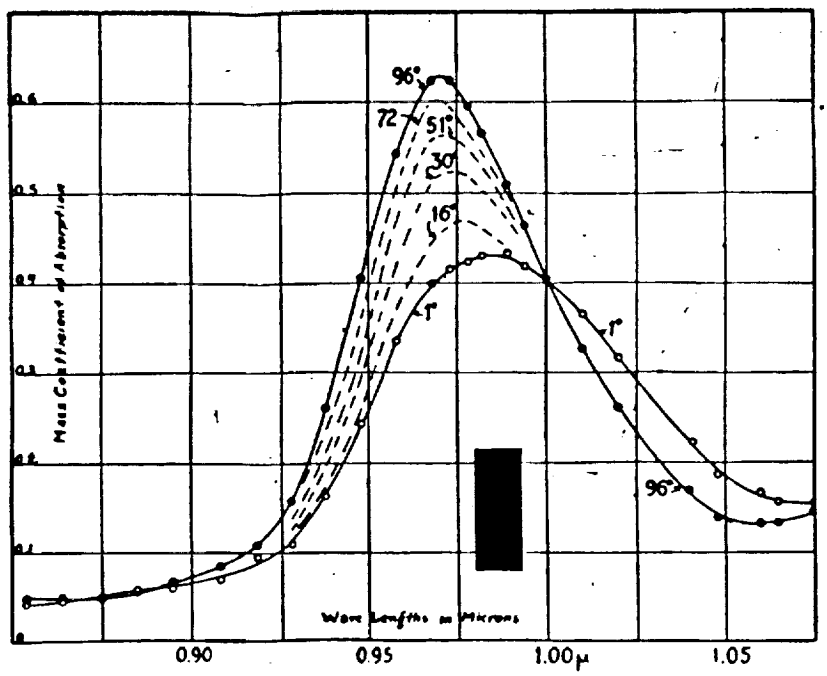


Figure 5. Absorption bands of water at varying temperatures (C) over 900-1050 nm range. From Collins (1925).

(b) The physical structure of the hot water. Even at the vent orifice, there is some entrainment of cold water, giving a turbulent plume with rapid changes in temperature and hence in refractive index across its width. In some vents, there is evidence in addition that there may be phase separation that produces relatively fresh and relatively salty fluids (Butterfield et al. 1990), again giving rise to rapid variation in refractive index within the vent. Such complex structure in vents where, instead of a homogeneous fluid there is a turbulent heterogeneous fluid, reduces the transparency of the water and may enhance emissivity. Such enhancement would depend on the scale of the structures in the water and would need to be determined empirically. Similar enhancement would arise from small particles of sulfide in the hot water.

Both of these effects will complicate interpretation of remote multiband images of hot vents and require empirically-determined corrections.

Studies of supercritical water oxidation may be carried out in the laboratory using a high-pressure (450 bars), high-temperature (600°C), saline tolerant optical cell (Tester et al 1991; Armellini and Tester 1991). The properties of water and aqueous sodium chloride solutions in the near- and supercritical regions may in fact be highly relevant to processes occurring at the vents or in the chimneys. In addition to laboratory tests mentioned above, it is ultimately necessary to measure the emissivity of the hot turbulent seawater directly. One of the instruments described below, a dual optical fiber spectrometer, is capable of directly measuring the optical properties of the vent water and, hence, its emissivity as a function of wavelength.

Refractive Processes - Mirages

Hot seawater at the vents can create mirages by refracting and scattering incident light. The refractive index of hot seawater differs from cold seawater, as does the salinity and turbidity. Hot water below the critical temperature of 374°C has a lower index of refraction than cooler water. At a pool of hot seawater under a flange, the refractive effect looking up is similar to that looking from water into air, with total internal reflection at angles greater than the critical angle. That is why these pools appear highly reflective when viewed from an angle, but can be seen through when looking directly up.

Turbulent jets should have similar refractive properties before they entrain enough neutral pH water to precipitate sulfides, etc., and turn black. Turbulent jets can be approximated by a cylindrical body where sighting normal to the jet and along the midline may permit one to see through the jet. A vertical gradient in index due to cooling will refract upwards, so that one may in fact see higher objects and the far lip of the chimney may not be visible. Sighting normal to the jet but at the edges, the critical angle will be exceeded and there will be total "internal" reflection, so the jet will appear reflective. Viewed from a location in between the edge and the midline, there will be some penetration through the jet, but the view will be over a smaller width than the actual width of the jet -- like the effect of looking at a face through strong myopic corrective glasses. There is little possibility that one could see into the chimney, given that the hydrothermal fluid is of lower refractive index than the surrounding water. Supercritical conditions complicate this interpretation of apparent transparency of vent water under specified viewing conditions and indicate the need for careful *in situ* observations of optical parameters at vents that are potentially supercritical. At the critical temperature, the dielectric constant of water changes, water becomes non-polar, and the index of refraction may change greatly and may fluctuate wildly over short distances. This may cause different optical refractive effects at the smokers where the exit temperature is supercritical. There may be critical point opalescence where the transition occurs, making the water appear white under external illumination. Turbulent flow will change the interface dramatically and mask many internal/external contrasts.

Refractive effects are ultimately related to the blackbody emissivity discussed above. Videos of illuminated vent water which show these scattering and mirage effects can provide some indication of the physical conditions of the vent water. For example, a video has been obtained showing the image of a background scene reflected off a stagnant inverted pool of hot seawater. As the angle of the camera is changed the

reflection angle changes at a different rate. At the critical angle, the refractive index of this hot vent water could be obtained directly, using Snell's law, from these video images. Another example may be found in some videos taken of the turbid vent water. They show the scattering and mirage effect mentioned above, and suggest that the turbulent vent water may in most cases have a high optical depth in the visible part of the spectrum, but this interpretation might change if the fluids were in a supercritical condition. Quantitative measurements of these effects would go a long way towards constraining the actual range of emissivity of hot vent water in the important green part of the spectrum.

A.1c. Potential Sources of Light Superimposed on the Thermal Radiation Spectrum

We considered sources of light that could exist in black smokers in addition to "black body" radiation, focusing on known mechanisms that have been demonstrated in solutions. In this section, we discuss types, mechanisms, and spectral signatures that could be looked for in the undersea environment. It is quickly apparent that *in situ* spectral measurements are critical because the spectrum will distinguish supplemental light sources from blackbody radiation if the spectral intensity of light produced by supplemental mechanisms is greater than or equal to that of the corresponding spectral black body emission.

The mechanisms discussed below are listed in order of their likelihood of contributing significantly to the light emitted by the black smokers, in excess of that emitted in blackbody radiation. The most likely source of excess light is from crystalloluminescence. The phenomenon has been observed by eye in the laboratory in hot water using chemicals that are known to exist in hydrothermal plumes. Other possible light sources are discussed and their properties are described. Whenever possible we suggest spectroscopic experiments that would distinguish the emitted light from blackbody radiation. A technical report generated subsequent to this workshop provides further review of possible sources of non-thermal low-level light emission (Reynolds 1993).

Crystalloluminescence.

Crystalloluminescence (XTL) is defined as the emission of light that occurs at the onset of crystallization. The first reported observation of XTL, that of potassium sulfate crystallized rapidly from water, was reported in the eighteenth century (Harvey 1959). Other substances that exhibit XTL include sodium sulfate, potassium hydrogen sulfate and cobalt sulfate. Although a detailed mechanism has not yet been proposed, the experimental results obtained to date are consistent with emission from defect or impurity luminescence centers that can be excited by the energy released during nucleation or crystallization. The XTL mechanism produces light intense enough to be visible to the eye in a dimly lit room. The only known spectra were reported in 1982 (Zink et al. 1982; Figure 6). The spectra had their band maxima in the visible region of the spectrum. All known examples consist of broad bands (on the order of 100 nm.) The spectra extend to wavelengths longer than 600 nm. They can be distinguished from black body radiation consistent with temperatures known to exist in black smokers because they peak in the visible region and decrease rapidly in the near IR region. XTL occurs from microcrystals that may be smaller than the wavelength of visible light (i.e. too small to be seen by the naked eye).

In the cases of the compounds that have been studied, the XTL spectrum was very similar to the photoluminescence spectrum excited with ultraviolet light. Thus a simple method to determine the potential wavelengths at which this phenomenon could occur would be to collect samples of the solids from the plume and measure the photoluminescence spectrum in the laboratory. A second experiment would be to excite the plume directly with UV light and to measure the photoluminescence emission spectrum. Crystalloluminescence could be a significant contributor to the light emission from the plume. Sulfate salts are known to be XTL active and are known to exist in the plume. In addition, metal sulfides are known to be good phosphors and are a major constituent of the plume. (XTL from metal sulfides has not yet been tested.) In small beakers in the laboratory, the duration of XTL is dependent on the rate of crystallization (i.e. on the rate of cooling) and can persist for minutes. The observer sees individual flashes of light as

the crystals form. In the plume where the rate of temperature change is fast as the column rises and the replenishment of the materials is continuous, it is possible that a quasi-continuous emission would be observed. It will be important to observe the light at the plume by using a detector that can time-resolve microsecond events. XTL may appear as individual flashes consisting of more than one photon corresponding to individual crystallization events, whereas black body radiation would be the smooth arrival rate of individual photons on time scales of second and longer.

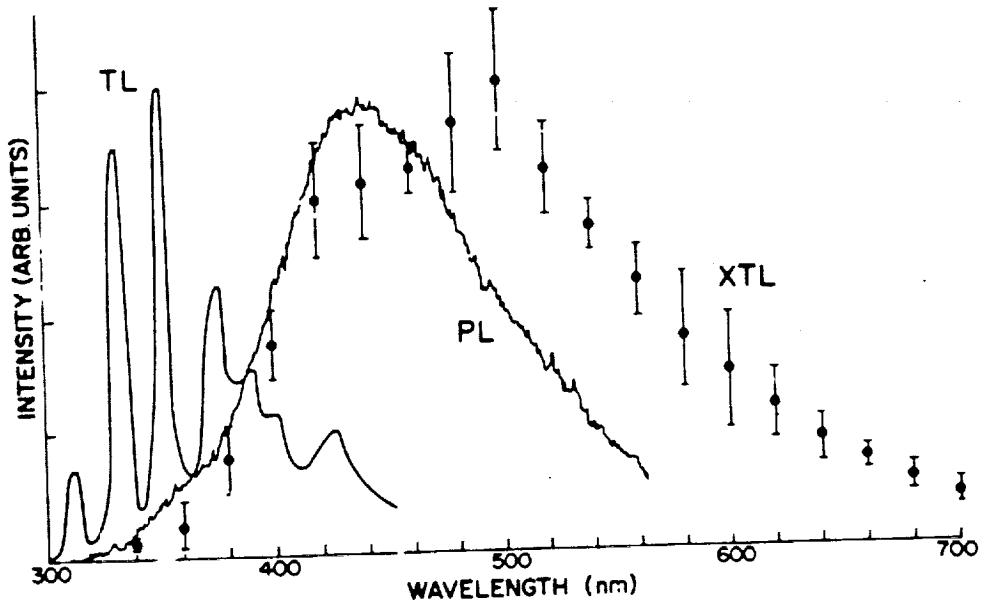


Figure 6. Crystalloluminescence (XTL), triboluminescence (TL) and photoluminescence (PL) spectra of barium chlorate [$Ba(ClO_3)_2$]. The XTL spectrum was obtained by placing a hot, saturated aqueous solution in a cooled sample holder. The triboluminescence spectrum was obtained by grinding the solid in front of the entrance optics of the spectrophotometer. The photoluminescence spectrum was generated by irradiance and spectroscopy. The XTL spectrum consists of a broad band centered at 490 nm; this spectrum is consistent with emission from a defect or impurity luminescence center which can be excited during nucleation or crystallization. The TL spectrum originates from nitrogen emission, where the nitrogen is of atmospheric origin. From Zink 1982.

Luminescence Associated with Ionizing Radiation

Light generation from radiaoactive decay is also likely to contribute to the visible flux at vents. The dominant mechanisms are Čerenkov radiation emitted by beta decay electrons traveling faster than the velocity of light in seawater (typically those with kinetic energies of 0.3 Mev or more), and scintillation in sulfide minerals (note that zinc sulfide, a common hydrothermal mineral at deep sea vents, is the material used to detect alpha particles by Rutherford at the turn of the century). Of these, beta decay may occur anywhere in the vent field or surrounding waters, while scintillation would be expected around sulfide chimneys or precipitating minerals. Čerenkov light is most intense at the short end of the visible spectrum where thermal radiation is comparatively weak. K^{40} beta decay generates a visible photon flux on the order of 1.2×10^6 photons m^{-2} sec^{-1} (Bradner et al. 1987; figure X) everywhere in the ocean and serves as a lower limit for deep-sea visible light. This level of light is at the threshold for biological light detection. Vent

fluids are often enriched in radium (and its decay product, radon) by factors of 20-200 over normal seawater (Kadko et al. 1988) resulting in enhanced radon concentrations throughout the vent field (Rosenberg et al. 1988). Rn^{222} is a particularly energetic (3.3 Mev kinetic energy) beta emitter which can as much as double the local Čerenkov photon flux.

Chemiluminescence

Chemiluminescence (CL) is the conversion of chemical energy to light energy. The chemiluminescent reaction produces molecules in excited electronic states that emit light. Frequently the CL spectrum matches the photoluminescence spectrum of the product molecule. Chemiluminescence is known for a variety of organic molecules as well as for simple molecules such as HCl and H_2O. The spectra can be broad bands (greater than tens of nm) that peak in the visible region of the spectrum. Because of the presence of efficient radiationless deactivation pathways under the temperature and pressure conditions of the plume, this mechanism may not be significant.

Triboluminescence

Triboluminescence (TL) is the emission of light caused by the application of mechanical energy to a solid (Zink 1981). In most of the cases that have been studied, crystal fracture is required. A very large number of salts, including sulfates, are TL active (Zink et al. 1980). The light is intense enough to be detectable by eye in a dimly lit room. TL induced by thermal shock is known. TL has not been demonstrated under the temperature and pressure conditions of the plume. However, because many of the solid constituents of the black smokers are known to be TL active, this mechanism must be considered.

Sonoluminescence

Sonoluminescence, (SL), is the emission of light caused by the implosion of a bubble in a liquid (i.e., cavitation). When seawater is subjected to ultrasound (20kHz) visible light is emitted. The spectrum consists of a broad band with a pronounced peak at 589 nm assigned to the emission of excited state sodium atoms (Becker et al., 1992). In water containing higher concentrations of other alkali metal ions such as potassium, lines at other wavelengths are seen. It has been reported that water containing elemental sulfur exhibits SL with a characteristic band at 920 nm. SL has only been demonstrated for bubbles less than about 100 mM. It has not been observed for macroscopic bubbles such as those produced by propellers. The existence of a SL mechanism could be demonstrated by the presence of a pronounced peak at 589 nm in the emission spectrum of a vent. Such a source of light in seafloor hydrothermal vents would be expected to be quite dependent on the physiography of the local ridge environment. For example, multiphase fluids would not be expected to vent from relatively deep ridge sites, but could occur in shallower systems. Secondly, magmatic activity and shallow magma chambers result in relatively high temperatures of venting (Von Damm et al. 1991, 1992) and, potentially, supercritical solutions. Exactly how such conditions could create bubble implosion and thus SL, needs to be explored to evaluate this mechanism for contributions to overall light emission and effective observation options. A more detailed evaluation of the potential for sonoluminescence is provided in Appendix II.

Burning of Methane in Supercritical Water

High temperature fluids can discharge from hydrothermal vents in the range of 300-400°C, which is in the near-to-supercritical range for water (e.g. Simoneit, 1992). The critical point of fresh water is ~370°C at ~300 bar, while vent solutions will exhibit a critical composition range dependent on composition, approximated by nominal seawater at 402°C and ~300 bar. Vent fluids contain significant and variable amounts of methane and carbon dioxide. Both these compounds in the pure state are supercritical at temperature and pressure conditions typical seafloor vents. The influence of these compounds on the critical point of solutions in a ternary mixture is not known but suspected to lower the critical temperature. Methane burns with a yellow flame in supercritical water in the presence of dissolved oxygen (Shaw et al. 1991). The visible spectrum and other physical parameters should be obtained from the laboratory experiments and compared with the data from the vents to see if it is feasible for a "flame" to occur at the mixing interface of hydrothermal fluid containing methane and oxygenated seawater.

Bioluminescence Background

Bioluminescence can be measured at any depth in the ocean, up to ultrabyssal (Bradner et al. 1987). Its intensity decreases with depth, however, roughly by a logarithmic law. The contribution of bioluminescence to the ambient light regime at hydrothermal vents is unknown; bioluminescence has yet to be rejected as the stimulus for vision in the unusual eye of *Rimicaris exoculata*. It is highly probable that against the background of scarce bioluminescent activity in the deep-sea plankton, enhancement of bioluminescence may be associated with hydrothermal communities. Time-series measurements of bioluminescent light by a spatial array of bathyphotometers equipped with mechanical or hydrodynamical stimulators would permit evaluation of the significance of bioluminescence within the context of the overall photic environment of hydrothermal vents. Potential interrelations between bioutilization of bioluminescent light sources and light emitted from high temperature vents need to be considered.

Non-blackbody sources of light will in most cases appear as broad (>10 nm) peaks in the visible region of the spectrum, in contrast to the unimodal spectral curve characteristic of blackbody radiation. In addition to spectral analysis, time-dependence of emissions may provide a distinguishing feature of many non-blackbody sources. In the cases of crystalloluminescence, triboluminescence, and sonoluminescence, the emitted light will consist of individual events of more than one photon each discernible over micro- or milli-second intervals. Longer duration measurements may prove useful because the intensity of blackbody radiation may be modulated by fluctuating emissivity due to turbulent mixing of hot vent water with cold seawater and fluctuating salinity gradients over time scales of seconds. Other mechanisms could result in short time-scale changes, such as fluctuations in the chemical content of the water.

A.2. Instrumentation and Technique Development

Preliminary physical and biological observations, together with consideration of the optical properties of vent water and of other possible sources of ambient light in hydrothermal systems, provide the context for the design of instrument packages to characterize the vent light.

Ultra-low light level CCD detectors are used routinely in astronomy to study galactic phenomena; we have the opportunity to apply this state-of-the-art technology to resolve the spatial, temporal and spectral characteristics of ambient light at hydrothermal vents. Requirements for spectral resolution extend from visible (450 nm) to near-infrared (1050 nm) wavelengths. At distances greater than 10 cm, seawater effectively cuts off wavelengths in the near-IR longer than 850 nm. But for characterization of light quality within centimeters of a high-temperature thermal radiation source, spectroscopic instrumentation should have a spectral sensitivity extending over the additional range of 850-1050 nm.

Several instruments are required to cover imaging and spectroscopy needs:

- Multi-band CCD Imaging and Low Resolution Spectrograph Camera
- Fiber-fed 400-1100 nm Low Resolution Spectrograph
- Time-resolved Green Light Survey Instrument

A.2a A Multi-Band CCD Imaging and Low Resolution Spectrograph Camera

A critical requirement is for a photometric test of the possibility that there are sources of luminosity other than blackbody at high temperature hydrothermal vents. A blackbody spectrum (emissivity of source independent of wavelength) has a known spectral shape, such that the ratio of photon flux from a blackbody at two different wavelengths is predictable. By taking the ratio of total flux collected through several filters with widely spaced bandpasses over the 400-1100 nm range, the blackbody nature of the source can be tested independent of absolute luminosity. Can CCD imaging through a set of bandpass filters test with

precision the hypothesis that there is no other source of luminosity at the vent other than that of a 620K blackbody? The sequential filter observations which have already been carried out are suggestive that the majority of the photon flux is that of blackbody radiation from the hot vent water. But the time scale for variation in the vent luminosity is known to be shorter than the time required for changing filters in a sequential expose - readout - change filter - expose scheme as was used in the first observations. Thus interpretation of the photometry in this sequential exposure scheme is seriously compromised.

It is crucial to have simultaneous multiband CCD imaging. This requirement can be incorporated into a redesigned CCD camera system. While a complete spectrum of the vent light with 1-5 nm resolution is required to reveal the process giving rise to any extra light over blackbody, this simultaneous imaging observation has the potential of revealing the position of the source of any excess light. Moreover, with the addition of a grating-prism to this system, it becomes a high-throughput, low-resolution spectrograph. This modified instrument could take simultaneous multiband images of the vents and then switch to the spectrograph mode and obtain a spectrum of the hot spots. A grating-prism spectrograph of this type is used in astronomy, where maximum throughput is required. Throughputs in excess of 40% have been obtained.

A.2b Spectroscopic Instrumentation

i Low Resolution, Fiber Optic-Fed Spectrometer

There is a need to determine the spectral distribution of various emission sources at high temperature plumes in order to determine their origin. A simple, robust, yet highly sensitive instrument is required, given the expected low emissions.

The recommended instrument uses a fiber optic probe that can be positioned near and at precise radial offsets from the vents and other arbitrary locations to control the light emission being sampled with precision. The fiber optics would conduct light to a compact, low resolution spectrometer. A precision CCD detector would be used to simultaneously quantify the light over the full spectral range of the spectrometer. The anticipated spectral range for this instrument is 400 nm to 1100 nm. This is based on a combination of the spectral transmission window of sea water convolved with the black body radiation from thermal vents and any other expected sources of luminescence. The spectral resolution requirements are modest, approximately 1 to 5 nm, due to the broad nature of any expected spectral features.

The optical spectrometer is envisioned to be derived from a standard commercially available compact spectrometer with the normal slit replaced by a multi-fiber feed. The detector could also be derived from a commercially available detector system. The digitized intensity data would be stored locally, and/or transmitted to the operators in the submersible or the surface ship. To estimate if the low resolution spectrometer envisioned would have adequate sensitivity to quantify the emission from the thermal vent, a computation was made on the following assumptions: The emission from the vent is that of a black body with an emissivity near 1. The fiber optic was assumed to have a numerical aperture of 0.3 and would be placed within a few centimeters of the vent jet The net throughput of the total fiber optic and spectrometer combination was arbitrarily chosen to be 0.1. The quantum efficiency of the detector was typical of a frontside illuminated CCD. The net signal at the detector at several wavelengths would then be:

(nm)	signal (electrons pixel^{-1} s^{-1})
600	1×10^{-3}
700	1
800	10^2
900	10^3
1000	10^3

The CCD detector readout noise could be approximately 5 electrons and the dark current 0.1 electrons pixel^{-1} s^{-1} (at -45°C). Based on these calculations, spectra of high signal to noise ratio can be measured between approximately 650 nm and 1050 nm using practical integration times of 1000 seconds and less.

One of the important operational considerations of this system is the ability to place the fiber optic probe at variable positions near any source of interest with precision. It will be necessary to place the probe such that it remains positionally stable for the duration of a measurement sequence. The fiber probe could be mounted to a stable platform, such as a tripod, near the vent and have provisions for motorized fine position adjustment. The fiber optic probe would also have an integral temperature sensor in order to determine the temperature of the zone under observation and to ensure that the probe is not damaged by exposure to extreme temperatures. A fiber optic probe constructed of robust materials such as fused silica and polyimide should be quite tolerant to high temperatures (as high as 400°C), but the corrosive nature of the vent effluent may have unpredictable effects. If the probe is damaged, the instrument should be designed in such a way that the probe can be easily replaced. Samples of optical fiber probe should be subjected to the hydrothermal vent environment as a test.

The capabilities of this same basic instrument could be greatly enhanced by adding provisions for optical stimulation of the probed area. This would be used to measure fluorescence and phosphorescence from both biological and mineral sources. The excitation source might be a simple low-power line source, such as a small, low-pressure mercury discharge lamp with a 254 nm filter. This would be coupled to a second fiber optic that would be routed adjacent to the input fiber bundle and illuminate the area directly in front of the fiber. The same spectrometer would be used in another configuration to indirectly determine the emissivity of the vent water as a function of wavelength. A source with several spectral lines throughout the visible and near-infrared wavelength, such as a neon discharge lamp, or an incandescent continuum source would be placed such that the spectrometer would measure the light transmitted through the vent jet (this could also be accomplished by routing the light using a fiber optic bundle). The absorptivity as a function of wavelength will be directly related to the emissivity of the jet as a function of wavelength. Knowing this and the jet temperature, the optical brightness of the jet as a function of temperature can be calculated and compared with actual measurements recorded directly by the spectrometer. Any radiation in excess of the grey body thermal tail from that vent would then be revealed.

ii Raman Probing for Dissolved Gases in Vent Environments

A second important class of spectroscopic measurements that would yield important scientific information is the quantification and speciation of inorganic species and dissolved gases by vibrational spectroscopy. Direct *in-situ* infrared vibrational measurements are not possible because of the aqueous environment, but Raman spectroscopy can be used to obtain essentially the same information. The optical configuration of this system would be nearly identical to the system used for fluorescence measurements. The only significant difference is that the spectrometer must operate at higher resolution over a narrower spectral range. A suitable Raman excitation source would be a solid-state diode source, coupled into the fiber optics delivery and light collection system envisioned as part of the CCD spectrometer; a filter would need to be added at the entrance to the spectrometer to block the light from Rayleigh scattering. The spectrometer could again be a commercially available unit but would need to work at about 0.1 nm resolution over a restricted wavelength interval of about 200 nm. The same focal plane detector system used in the low-resolution instrument above could be utilized for cost reasons if desired, and the data acquisition system would be identical.

The visible/near-IR spectrometer with fiber-optic probe to be deployed at the hydrothermal vents (see technical description above) offers an excellent opportunity for carrying out active spectroscopic sensing experiments at the vent environments. *In-situ* Raman probing for dissolved gases and inorganic ions would provide the capability of obtaining information on the abundance and distribution of these species in real time and with the spatial resolution afforded by the fiber-optic delivery system. Specific target system are

the dissolved gases O_2, CO_2, H_2S, H_2, and possibly methane and ammonia, all of which are key species in the chemistry and ecology of the vents. Raman detection of O_2 and CO_2 at millimolar levels in aqueous solution has been demonstrated by Feld and co-workers (Figure 7; unpublished) at the Harrison Spectroscopy Laboratory at M.I.T., using 514, 760, and 850 nm excitation wavelengths. Methane detection may be problematic, since its Raman-active, totally symmetric vibration may be obscured by the strong water bands near 3 micrometers, but background-subtraction techniques may permit its observation. *In situ* detection of sulfate ion may also be possible *via* its strong Raman transition at 987 cm^{-1}. In order to be able to interpret such spectra quantitatively, the effect of hydrostatic pressure on Raman band shapes for these species needs to be investigated in laboratory experiments.

A.2c Background Luminescence Survey

A need has been identified to survey the visible photon flux over a wide area in the vicinity of underwater hydrothermal activity. The purpose is to determine if there are widespread sources of low-level illumination from bioluminescent or chemiluminescent sources. An array of photodiodes or photomultiplier tubes and a data logging system provide the essentials of an instrument appropriate for this objective. Deployment of such an instrument at various microhabitats within a vent field will provide a measure of available sources of blue-green radiation in the region of hydrothermal vents. Some accommodation for mechanical disturbance may be required to stimulate *in situ* bioluminescence. Spectral information should be of limited value since the sources of light are expected to be a sufficient distance from the detector that wavelengths longer or shorter than the peak transmission of seawater will be severely attenuated.

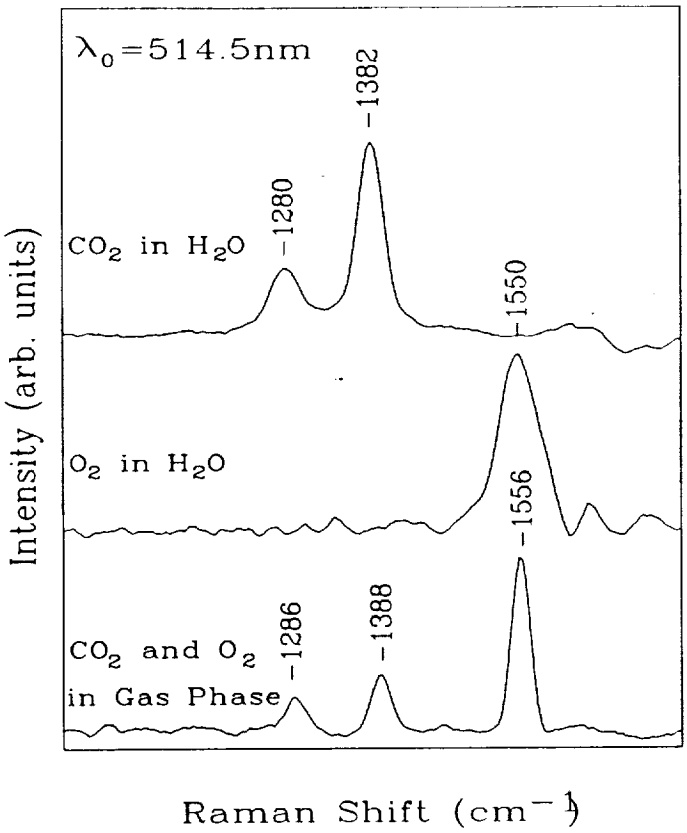


Figure 7. Raman shifts of CO_2 and O_2 in aqueous solution. M. Feld, Y. Wang, R. Dasoni et al., unpublished data.

A.2d Physical Structure and Ranging

Measurements of light at seafloor hydrothermal vents have demonstrated the temporal variability of the signal and dependence of the measurements on distance from the high temperature vents. While the initial measurements provide valuable information with only crude estimates of distance and stability of the measurement platform, future high precision data requires a method of determining spatial relationships of the source and detector with sub-centimeter accuracy.

A.2e Thermal Tomography

It may be possible to reconstruct the 3-dimensional temperature structure of the thermal vents as a function of position T(r), where r is a 3-dimensional vector using acoustic techniques. The basic method assumes that radiation from thermal vents can be attributed to some material, (water + other substances) and that the relationship between the amount of radiation being emitted from the vents as a function of temperature is known, E(T,r). Given the radiation law (revised blackbody relationship), and the observed radiance around the vent field, it might be possible to reconstruct the 3-dimensional temperature profile.

This problem is actually very similar to one that is encountered in standard medical tomography: CAT (computer axial tomography), and ECT (emission computed tomography) (Kak and Slaney 1987). What is slightly different is that, in this case, the inversion is for the emission of radiation. Assuming a continuous distribution of sources and absorbers, the equations of radiative transfer dictate that the amount of radiation received by a sensor (that amount is fluxing through a given volume) will be a result of the passage of radiation from the sources minus the fraction that is absorbed and scattered in the interim paths. Even though the relationships are exponential, taking the logarithm of the recorded data (the radiometric flux) leads to a system of linear equations in which the unknowns are the attenuation and scattering coefficients.

It might be possible that a true 3-dimensional inverse can be constructed which includes the magnitude of the emitters and also the properties of the medium (absorption and scattering). This would have to be an area of future research. However, with some small amount of simplification, the problem is likely to be tractable. For example, assuming that the attenuation and scattering coefficients are radially symmetric about the vents would allow a great simplification of the number of unknowns. What makes this approach reasonable is the fact that the location of the vents can be clearly discerned. Then, given the above relationships between thermal emission and the proposed temperature, a forward model would be constructed which would predict the amount of radiation that is being recorded. As is typical in the solution of these inverse problems, the unknowns would then be changed iteratively until a match between observed data and the measured data was obtained.

A 3-dimensional map of the thermal structure of a vent might be obtained by using a form of tomography which assumes that the black-body law for deep sea vents is known. This would have to be either theoretically derived, or measured experimentally. Given this knowledge and some *in situ* sampling techniques which would allow measurement of the medium attenuation, the problem of inverting for the 3-dimensional structure can be posed as an inverse problem. Various methods have evolved over the years to solve inverse problems; application of these methods can be used to solve this very interesting problem in vent thermal radiation.

B. THE POTENTIAL FOR GEOTHERMALLY-DRIVEN PHOTOSYNTHESIS

Documentation of a source of geothermal light in the deep sea raises the issue of the potential for geothermally-driven photosynthesis (GDP) on the seafloor. Discussion of GDP at deep-sea hot vents is strictly hypothetical and further evaluation of this hypothesis depends critically on collection of accurate data regarding *in situ* light intensity and energy availability or direct evidence of the existence of phototrophs at vents. The discussion below is constrained by values for photon fluxes calculated from images of *in situ* ambient light obtained with a CCD camera that was sensitive to wavelengths up to 900 nm and on calculations based on theoretical consideration of 350°C black body radiation. Because of the expected very low light intensities, the productivity of phototrophic bacteria in the vent environment, if they exist, would be marginal compared to productivity of endosymbiotic and free-living chemoautotrophic bacteria. However, if photosynthetic bacteria are found in deep-sea hydrothermal environments, this could have great impact on our ideas of the evolution of photosynthetic systems. And if such photosynthetic bacteria do exist, physiological and biochemical adaptations that facilitate their predicted highly-efficient light-harvesting capacity and economy of energy utilization will be of considerable interest.

B.1a Light and Light Requirements by Phototrophic Bacteria at Hydrothermal Vents

i Light at Vents

The documented light at hydrothermal vents is predominantly wavelengths of 700 to 900 nm. These wavelengths are constrained at the longer wavelengths by the sensitivity of the CCD camera and at the shorter wavelengths by filter experiments. Photon flux calculated from values observed by the CCD camera in this wavelength band is 10^{10} photons m^{-2} sec^{-1} at 50 cm from the plume to 10^{13} photons m^{-2} sec^{-1} at 5 cm. So far light has only been observed at the jet of a high temperature vent. If this light is caused by thermal radiation, we expect emission of photons at wavelengths longer than 900 nm. If the source is an ideal blackbody at 350°C surface, fluxes within the 950 to 1050 nm band are on the order of 10^{16} photons m^{-2} sec^{-1}. Assuming an area of radiating surface of 0.001 m^2 and taking into account the absorption of light by seawater, the photon flux at wavelengths between 990 and 1060 nm reaching surfaces 0.5 cm distant would be 3.4×10^{16} photons m^{-2} sec^{-1}. Surfaces 5 cm distant would receive 2.5×10^{15} photons m^{-2} sec^{-1}.

ii Minimum Light Requirements by Phototrophic Organisms

Eucaryotic algae have compensation points ranging from 2 to 6×10^{18} photons m^{-2} sec^{-1} (Richardson et al. 1983). Anoxygenic phototrophic bacteria can grow at significantly lower light intensities. Observed requirements are 1.5×10^{17} photons m^{-2} sec^{-1} for laboratory cultures of the green sulfur bacterium *Chlorobium phaeobacteroides*. This organism was found at a depth of 80 m in the Black Sea. At this depth, the estimated light intensity was 2×10^{15} photons m^{-2} sec^{-1}. The calculated minimum doubling rate of *C. phaeobacteroides* under autotrophic growth conditions at this location would be almost 3 years (Overmann et al. 1992). If acetate is present, the doubling time would be much shorter, on the order of 4-7 months (van Gemerden, pers. comm.) As far as we know, this light intensity of 2×10^{15} photons m^{-2} sec^{-1} is the minimum claimed for photosynthetic growth. Phototrophic purple bacteria have photon requirements at least one order of magnitude higher than those of green sulfur bacteria (Biebl & Pfennig 1978, Eckert et al. 1986, Veldhuis & van Gemerden 1986).

Some purple nonsulfur bacteria containing bchl*a*, such as *Rhodospirillum rubrum*, have been grown in a chemostat at a specific growth rate of 0.1 hr^{-1} and a mean irradiance of 1.2×10^{19} photons m^{-2} sec^{-1}. Under these conditions, mean irradiance less than 1×10^{19} photons m^{-2} sec^{-1} would not support growth (Göbel 1978). Growth of *Thiocapsa roseopersicina* was found to be marginal at 1.2×10^{18} photons m^{-2} sec^{-1} (Veldhuis & van Gemerden 1986). Minimal light requirements for these bacteria, as for those having bchl*b*, are likely to be in the order of 10^{17} to 10^{18} photons m^{-2} sec^{-1}.

We can estimate a minimal photon requirement of an ideal photoautotrophic organism. Consider a spherical cell with a 1 μm^2 cross-sectional area, which typically contains ~20 fg carbon (Waterbury et al. 1986), with a theoretical requirement of 4 photons per carbon fixed (Mauzerall 1990). For a doubling time of one year and assuming a quantum efficiency of 100%, the photon flux requirement is 1.3×10^{14} photons m^{-2} sec^{-1}. Given the ideal assumptions, this result is consistent with the observed minimum photon requirement of 2×10^{15} photons m^{-2} sec^{-1} estimated for the *C. phaeobacteroides* in the Black Sea. Photon fluxes at or below this level imply chemotrophic growth.

Light requirements for photosynthesis might be satisfied by the calculated 350C black body radiation at wavelengths of 900 to 1100 nm, implying that photosynthesis could be possible at deep-sea hydrothermal vents.

B.2a Properties of Phototrophic Bacteria Compatible with the Vent Environment

If phototrophic bacteria are present in the vent environment we expect them to be of a very special kind and to have adapted through evolution to this particular habitat. The organisms might differ from all phototrophic bacteria we know so far and could have the following properties:

1. Pigments with absorption maxima above 700 nm. Because of the expected light available at the vent sites and because of the spectral light requirement of algae and cyanobacteria (chl *a* and *b*) and halobacteria, these organisms are most unlikely to be found there. For the same reason all bacteria with bchl*a* or bchl*b* (purple bacteria), bchl*g* (heliobacteria) and bchl*c*,*d*, or *e* (green bacteria) would be more likely candidates. Absorption spectra of bacteriochlorophylls are distinctive, with maxima at longer wavelengths than chlorophyll (Figure 8) .

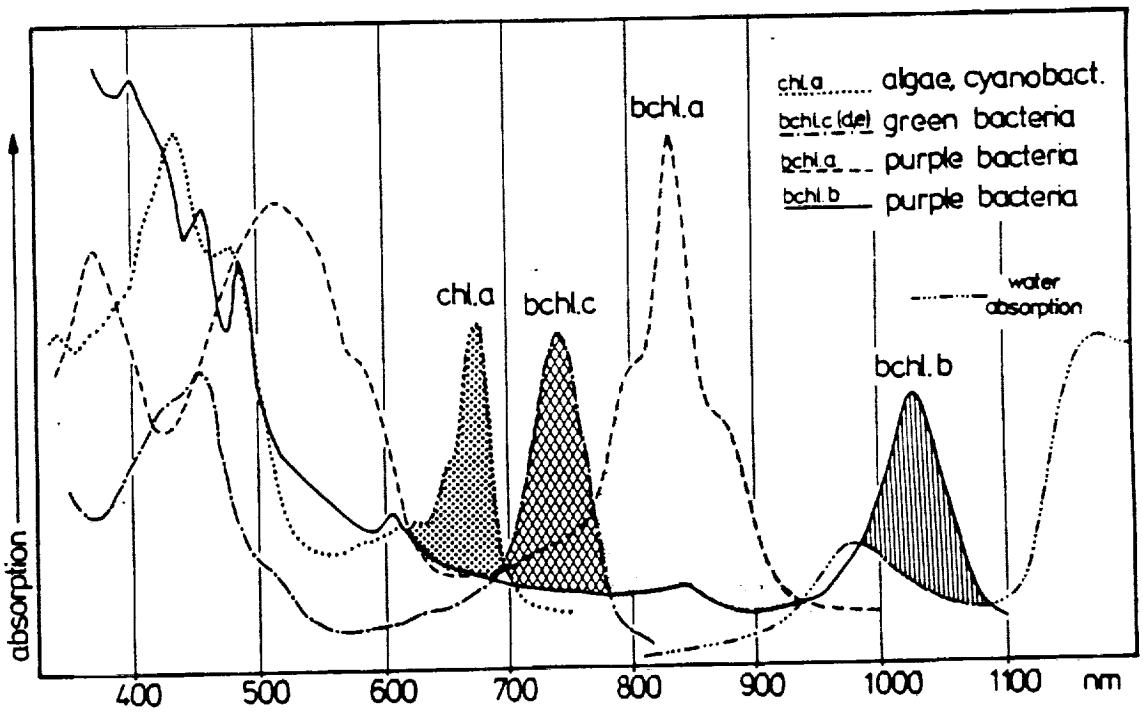


Figure 8. Absorption spectra of bacteriochlorophylls. From Pfennig 1989.

2. Ability to grow at extremely low light intensities. Because of their very efficient light-harvesting ability, green sulfur and green nonsulfur bacteria, which have highly developed light harvesting devices (chlorosomes) are considered to be likely candidates. They have their long wavelength absorption maxima between 700-760 nm. Although light harvesting and general efficiency in purple bacteria are lower than in green bacteria, the increased availability of light at longer wavelength may compensate for this shortcoming. In this regard, purple bacteria with absorption maxima above 900 nm are of particular interest. Species such as *Chromatium tepidum* (Madigan 1986) which has bchl*a* with an absorption maximum at 920 nm and all bchl*b*-containing species with maxima around 1020 nm would be included (Imhoff 1992, Pfennig 1989). Quite likely, phototrophic bacteria adapted to the very dim light of the vent environment would be very sensitive to light and may be inhibited even at relatively low light intensities.

3. Possibly thermotolerant or thermophilic. Thermophilic representatives from all groups of phototrophic bacteria with an upper temperature limit around 70C are known (Pfennig 1989).

4. Low maintenance energy requirements. Bacteria with chlorosomes have a lower maintenance energy requirement than purple bacteria (van Gemerden 1980). The latter have a large membrane surface which increases the probability of proton leakage (Raven & Beardall 1981). In addition, the formation of internal membranes requires higher energy expenditure for the production and maintenance of greater amounts of lipids and proteins produced (Ormerod et al. 1992). The chlorophyll can be packed more densely in the chlorosomes than in a membrane. Consequently, light harvesting by chlorosomes is more effective than by photosynthetic membranes.

5. Efficient biosynthetic metabolism. The biosynthetic metabolism of green sulfur bacteria is more efficient than that of other anoxygenic phototrophic bacteria. However, this efficiency is dependent upon oxygen-free growth conditions (Ormerod et al. 1992)

6. Use of H_2, sulfide, Fe^{2+}, FeS, or other reduced sulfur compounds as electron donors. Reduced sulfur compounds and H_2 are commonly utilized by anoxygenic phototrophic bacteria.

7. Possible use of simple organic compounds and ability to fix nitrogen. All known anoxygenic phototrophic bacteria can use various simple organic compounds, and most species fix N_2.

8. Tolerant to high sulfide concentrations (5-9 mM), to heavy metals, and pressure (250-350 atm depending on depth). Nothing is known about pressure tolerance of phototrophic prokaryotes. However, it is expected that pressure adaptation would not be critical. Green sulfur bacteria are among the organisms most tolerant to high sulfide concentrations.

9. Tolerant to oxygen, at least for short periods. Ecological niches for green sulfur bacteria are usually permanently anoxic. If the niche is one which is intermittently subjected to oxic conditions, one would expect the presence of a purple bacterium or a motile green bacterium. Actually, many purple bacteria can also grow chemotrophically, i.e. aerobically in the dark (Kämpf & Pfennig 1980, Kämpf & Pfennig 1986). They can be regarded as facultatively phototrophic bacteria and are well-adapted to changing environmental conditions.

As far as we know, none of the phototrophic bacteria that have been studied thus far would be perfectly adapted to live at deep-sea hot vents. However, we expect that only a fraction of the existing phototrophic bacteria are known and that some still unknown types may be better fitted to this environment. So far no phototrophic archaebacterium with *bchl* is known. Because of the higher temperature range of some archaebacteria, it is conceivable to consider the existence of such a bacterium in this environment.

In more general terms, a hypothetical vent phototrophic bacterium:

-- should be thermophilic, within the limits compatible with phototrophic metabolism
-- should have chlorosome-like or extended antennae
-- should preferably have bacteriochlorophylls absorbing at higher wavelength compared to bchl*c*,*d* and *e*. Because the chemical environment of *bchl* molecules (i.e. proteins, lipids, other pigments) determines the *in vivo* absorption characteristics, one can imagine a photosynthetic apparatus to have evolved in the hot vent environment which has absorption maxima at the wavelength most abundant at these depths. For example, bchl*a* pigment-protein complexes are known which vary in their long wavelength absorption maxima from 820 to 920 μm (Zuber & Brunisholz 1989).
-- could very well be facultative phototrophs, tolerant to oxygen and capable of chemotrophic respiration

B.2c Habitat Requirements

i Physical/Chemical Requirements for Photosynthesis

The two primary considerations for photosynthesis at deep-sea thermal environments are a source of light of suitable spectral quality and intensity, and temperature compatible with life. The known upper limit for photosynthesis is 70C to 74C for *Chloroflexus aurantiacus* and *Synechococcus lividus,* respectively. We should keep in mind that the current theoretical upper limit for life is considered to be 120 to 130C (Daniel 1992, Stetter et al. 1986).

Other habitat requirements that are expected to be easily satisfied include sufficient nutrients (N,P,S), electron donors (H_2, reduced inorganic sulfur compounds) and simple organic compounds such as acetate. The lower pH limits for photosynthesis are estimated at pH 4 for anoxygenic phototrophs.

ii. Potential Habitats

Given thermal radiation as the principal source of light energy and the absorption characteristics of light in seawater, potential habitats for photosynthetic microorganisms are confined to regions of steep thermal and photic gradients anticipated in certain microhabitats. Potential habitats include surfaces and pore spaces of precipitated sulfides. Anoxic microhabitats are likely niches, considering the photosynthetic efficiency of anoxygenic vs. oxygenic photosynthesis, but periodic exposure to oxygen would not exclude phototrophs, given various protective mechanisms for overcoming oxygen toxicity. Habitats to be explored include the interstitial spaces of subsurface sulfides. This could include depths below the seafloor from tens to hundreds of meters. To achieve the gradients of light and temperature, subsurface percolation bringing colder water in direct contact with the hot fluid would be necessary. While this is a relatively inaccessible environment, cores from drill holes in hydrothermal systems planned by the Ocean Drilling Program could provide precious material for a search for evidence of phototrophs. More accessible areas in which steep gradients are known to occur include the walls of black smoker chimneys and horizontal flanges, both of which might support endolithic phototrophic life. The only apparent epilithic sites include the very tops of chimneys and the edges of pooled hot water which collect underneath horizontal sulfide growths (flanges). One can even imagine phototrophs on the surfaces of deep-sea vent shrimp, *Rimicaris exoculata,* assuming the shrimp are continuously in close proximity to the glow of the hot smokers. In addition to thermally-associated light, diffusive hydrothermal environments, which may emit light as a result of chemiluminescence, might be examined for evidence of phototrophy. This includes surfaces of sediments and cracks in the basalts where warm water flow occurs.

The occurrence of endolithic bacteria has been noted for flanges at the Juan de Fuca vent sites. Both archaebacterial and eubacterial lipids have been profiled through a flange with a peak in archaebacterial lipids closer to the hot water source (Hedrick et al. 1992). Oligonucleotide probes were also used to detect both archaebacteria and eubacteria in these flanges, showing similar zonation.

Given the expected interaction of light with the sulfidic environments (high absorbance, reflection, etc.) we expect high attenuation of light and possible spectral shifts. These are likely to be in very small bands, and it will be necessary to survey these habitats on a very small scale, ideally in 100s to 10s of micrometers (Jorgensen et al. 1987) Light must be measured using an optic fiber, the tip of which has an integration sphere, i.e., summation of light from 360 degrees (Lassen et al. 1992). All other parameters must be examined at a similar scale using specific microsensors.

B.3 Recommendations

While it is premature to undertake a systematic search for phototrophs at deep-sea hydrothermal vents, there are several techniques that could readily be applied to samples of opportunity for indications of the presence of phototrophs. Bacteriochlorophyll pigments are diagnostic of phototrophs, so that pigment extractions of putative habitats (e.g. sulfide minerals) could screen for phototrophs. Putative habitats could also be subsampled for electron microscopy and a search for indicative ultrastructural details such as chromosomes in green bacteria and chromatophore membranes in purple bacteria. Application of PCR (Polymerase Chain Reaction) methods on samples of sulfides to amplify a conservative 10 amino acid stretch of all PS I systems and an analogous approach to amplify a conservative region of PS II systems, with subsequent *in situ* hybridization could be used to confirm presence of the gene. Biomarkers and DNA probes specific for phototrophic bacteria might also detect the presence of phototrophs in putative habitats. Attempts should also be made to isolate phototrophs from vent samples and culture them under varying environmental conditions.

Careful studies of available light intensity and its spectral distribution at the vent sites are highly desirable. These studies should include light penetration through sulfide minerals to determine the suitability of interstitial environments as habitats for phototrophs.

C. PHOTORECEPTION

Light from some source or sources exists at hydrothermal vents and certain vent species may have evolved novel organs to exploit that light. Several new species of shrimp have been discovered (Williams and Rona, 1986; Martin and Hessler, 1990) that have specialized arrays of photoreceptors seemingly derived from the eyes of common shrimp (Figure 9; Van Dover et al., 1989; Pelli and Chamberlain, 1989; Chamberlain unpublished). Characterization of the ambient light environment at hydrothermal vents, the structure and function of specialized photoreceptive sensory organs, and the adaptive advantage of these organs to the animal may lead to new insights about the adaptability of sensory systems as organisms occupy specialized niches, and about vision in general as vent species are compared with surface species.

Light sources at vents can be considered from the perspective of what we know about biological usage and strategies with respect to light in the oceans. Visual sensitivity of vent organisms may be taken as indicative of characteristics of the putative light source. From the evidence based on known parameters of the vent shrimp, *Rimicaris exoculata*, the "eye" (light-gathering organ) is characteristic of organisms which sacrifice resolution in order to maximize sensitivity. The structure of the light-gathering organ suggests orientation to a wide field source rather than point source and this orientation requires whole body movement. These features suggest a requirement for a source with relatively long emission kinetics. As a light sensitivity comparison, the human threshold for a large dim source of wavelength 507 nm is about 19.6 quanta per second per square degree for a long exposure. For a small spot of light, the corresponding threshold is about 100 to 150 quanta per second per square degree for a long exposure (e.g. Wyszecki and Stiles 1982). The apparent lack of response by these shrimp to the submersible's lights may be because they are actually blinded (possibly permanently) by such high intensities.

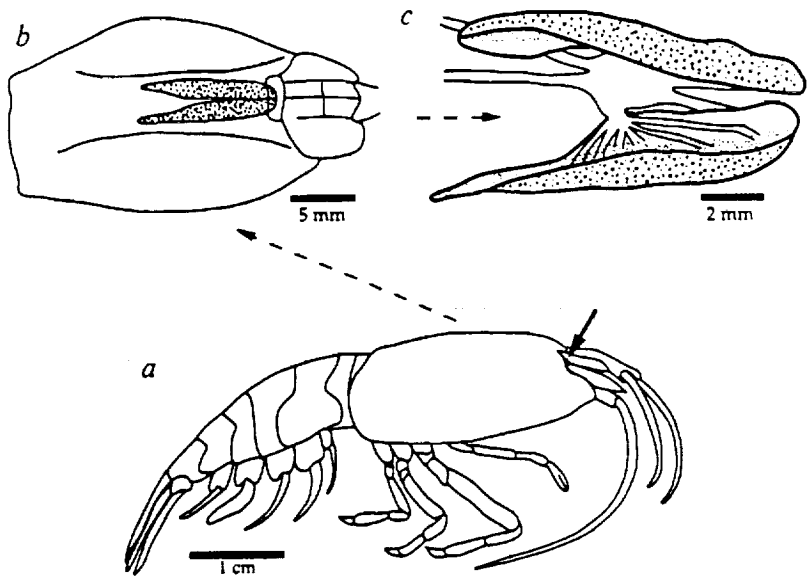


Figure 9. *Rimicaris exoculata.* a) lateral view. *R. exoculata* lacks eyestalks and conventional componènts of crustacean compound eyes. Solid arrow points to the location of eyes in the confamilial species *Chorocaris chacei*. *b)* Oblique dorsal view showing the location of the novel visual organ (stippled area) underlying the thin transparent carapace. *c)* Dissection of the thoracic eye. The fused anterior tips have been separated along the midline to reveal the underlying connections to the supraesophageal ganglion of the shrimp. From Van Dover et al. 1989.

Maximum sensitivity of most organisms living below the photic zone is closely matched to the wavelength of the predominant source of light, namely bioluminescence. In the open ocean, bioluminescence and visual sensitivity maxima are approximately 480 nm. In water where there is more particulate matter, green light penetrates better, resulting in both bioluminescence and visual sensitivity maxima shifting toward green. Present evidence indicates that green spectral sensitivity is enhanced in *Rimicaris exoculata* (Figure 10; Van Dover et al. 1989). At increasing distances from a hydrothermal vent, the diffuse attenuation of ocean water will shift the available spectral distribution; the further away, the better the match to the absorption spectrum of the rhodopsin extracted from *R. exoculata*. Thus, the "eye" of *R. exoculata* may be used for long distance detection of vents, providing orientation advantages over or in addition to chemoreception, especially if the predominant direction of flow is toward the vents.

The non-imaging "eyes" of *R. exoculata* (Figure 8) might be used to locate bioluminescence, but non-imaging "eyes" are generally highly integrative in both space and time, making transient emissions of most bioluminescent organisms less than optimal stimuli. Ambient light conditions at hydrothermal vents have not been explored beyond the light emitted from high temperature jets. It is possible that bioluminescence plays a more important role at vents than currently suspected. While observations from midwater submersibles indicate the absence of bioluminescence in midwater in the absence of stimulation (Widder et al. 1989, Widder et al. 1992), thermally-driven flow regimes at vents and complex bottom topography might provide natural stimulation of planktonic bioluminescence. Bacterial bioluminescence produces a

relatively constant glow under certain growth conditions (Haas 1980). *In situ* bioluminescent characteristics of vent bacteria are unknown. Do bacterial mats at vents glow? Perhaps shrimp locate bacterial mats to graze upon by detecting their glow. While an attractive hypothesis, the adaptive advantage of bioluminescence to the bacteria is problematic (Hastings 1978).

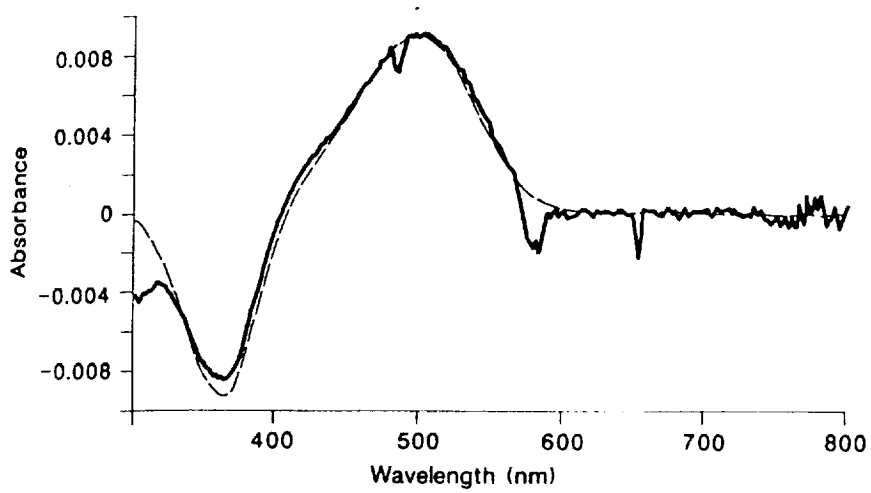


Figure 10. Bleaching difference spectrum of visual pigment in Rimicaris exoculata (solid trace), obtained by subtraction of spectra before and after belaching.Absorption due to reactants is positive and to products is negative. Bleaching destroys a shrimp pigment that maximally absorbs at 500 nm, typical of 'classical' rhodopsin, and creates a new pigment with an absorption maximum at 367 nm, which corresponds to retinaloxime. The same features are seen in the difference spectrum of frog rhodopsin (dashed line) normalized to maximum absorbance at 500 nm. From Van Dover et al. 1989.

Two aspects of light at hydrothermal vents are 1) total intensity and 2) wavelength distribution of the light. Total intensity is important when considering the possibility of photosynthesis in the vicinity of the vent. The wavelength dependence is important both for photosynthesis and for the possibility that the shrimp *R. exoculata* uses its photosensors to find vents and/or avoid the hottest parts of the vents. The possible use of the light for sensory cues opens an interesting avenue for speculation. The most important aspect of the emitted light may be the intensity of individual pulses, not the integrated intensity. A brief pulse of light containing many photons followed by a long period of darkness will have a very low apparent intensity when integrated over a time scale of minutes. However, the pulse may be more important to an organism that uses it for directional information than an equal number of photons spread out evenly over the same time period. The pulse height above the background may be of critical importance. This phenomenon is important in bioluminescence; the organism is usually dark and produces light pulses only when stimulated or when needed. The total integrated output is very small but the height of an individual pulse is large. Crystalloluminescence produces light in pulses. Each time a crystal is formed a pulse of light is produced. It is hard to imagine a better method of producing XTL than flowing hot, mineral-laden water into a cold reservoir. The unknown quantities in evaluating this mechanism are what crystals are actually being formed

immediately above the chimney of a black smoker, whether these solids are XTL active, and the rate of formation. If the rate of crystal formation is rapid, the individual flashes of light would occur so rapidly that an observer would interpret the light as continuous. On the other hand, measurement on the microsecond time scale could show sequences of pulses of varying heights characteristic of the formation of and emission by crystals of varying sizes and distances from the observer. The wavelengths of the XTL emission bands will depend on the nature of the crystals being formed. (The spectra of the few compounds that have been studied in the laboratory contain bands in the visible region of the spectrum.) Manganese(II) ions in tetrahedral environments generally emit in the green region of the spectrum. If these ions serve as activators, green emission may be common and may occur whenever Mn impurities are contained as impurities in the crystal or when a crystal of a manganese salt is formed. These occurrences may be sporadic. Thus, it is interesting to speculate that occasional, relatively intense pulses of blue-green light that penetrate relatively far through sea water are emitted by black smokers, and that *Rimicaris exoculata* uses these pulses for directional cues.

B.1a The Ambient Light Environment

Recent characterization of rhodopsin from the "eye" of *Rimicaris exoculata* and concurrent structural identification of an expanded photoreceptor array both strongly imply the existence of exploitable light in the hydrothermal vent environment, since in the absence of light, visual regression leads to the elimination or severe reduction of visual organs (Lythogoe 1979). CCD camera imaging of a black smoker from the Juan de Fuca Ridge confirms that hot vents are a source of light. The origin and nature of that light are problematic and themselves provide the rationale for lines of investigation. For interpretation of the sensory physiology of novel photoreceptors, we need an empirical description of the spectrum of light in the vent environment, including how the available spectrum changes with distance from the source in the hydrothermal fields.

B.1b Anatomical Studies

Preliminary anatomical information is available in the literature for the "eye" of only one vent species, *Rimicaris exoculata* (Van Dover et al. 1989; Figures 8, 10a). Information from this study, together with unpublished data on the eye of a second species, *Chorocaris chacei* (Figure 10b), suggest that the photoreceptor arrays in these species have evolved from compound eyes of related decapod shrimp. Common to these two vent shrimp eyes is the elaboration of light-catching membrane arrays, the shrinkage of the rest of the photoreceptor cell, the loss of optical structures to channel light, and the development of mirrors below the photoreceptor layer. These adaptations suggest that for these animals, high sensitivity detection of the direction of light sources in the environment has precedence over image formation.

There is a clear anatomical research agenda. First, potential difficulties from overly bright light exposure, overly large pressure changes and overly great temperature changes during collection must be evaluated and overcome (e.g. Chamberlain et al., 1986). Then, the structure and ultrastructure of the eyes of vent animals need to be described. The specially-adapted eyes of vent shrimp are a logical starting point, but ultimately the eyes of other crustaceans and vertebrates observed at vents should also be examined. Correlation of structural data from vent species with corresponding physiological and behavioral data will prove extremely useful in understanding how these animals exploit the unique photic environment around the vents.

Study of ontogenetic changes in the morphology of the photoreceptor in the shrimp may provide insight into how the major structural modifications in eye morphology are accommodated during development. The evolutionary derivation of the modified eye may be understood through ontogenetic and comparative anatomical studies of eyes in species belonging to the family Bresiliidae. This family is well-represented at deep-sea hydrothermal vents as well as at non-thermal "cold seep" environments such as the sulfide-rich brine seeps at the base of the Florida Escarpment. Members of this family exhibit a range of morphological

types from "normal" stalked compound eyes in *Alvinocaris lusca* (a species common at low temperature hydrothermal vents on the Galapagos Spreading Center), through intermediate eye morphs displayed by members of the genus *Chorocaris*, to the extreme derivation observed in *Rimicaris exoculata*. Wolsky and Wolsky (1991) suggest that in the case of *R. exoculata*, rudiments of the eye were "rescued by the organism which has found for them, suitably transformed in size, shape and position, a new, unexpected function, the perception of a radiation (infrared?) existing in its environment but totally different from the radiation provided by daylight on the surface of the Earth". Structural modification of the crustacean eye, to the extreme illustrated by adult *Rimicaris exoculata*, includes loss of the eyestalks. Inasmuch as endocrine organs of shrimp are normally located on the eyestalks, an understanding of the transposition of these organs is of considerable physiological and anatomical interest.

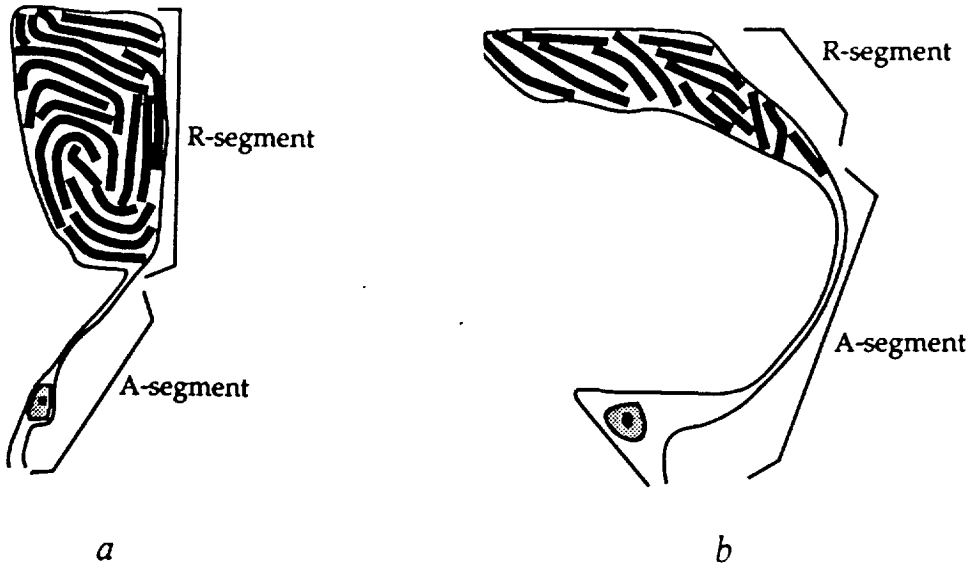


Figure 11. Photoreceptor cells from *Rimicaris exoculata* (a) and *Chorocaris chacei* (b). Compared to typical shrimp photoreceptors, these photocells have a hypertrophied light-sensitive rhabdomeral segment (R-segment) and an atrophied arhabdomeral segment (A-segment) which probably represent specializations for the light environment around hydrothermal vents or in the deep sea in general.

Comparison of structural data from the eyes of vent species of both invertebrates and vertebrates with corresponding species from the surface will provide information about evolutionary strategies employed in adapting to new photic environments. This work will also provide a clear comparison between visual systems adapted for the constant light environment of the hydrothermal vents and those adapted for the cyclic light environments of the surface (Hornstein and Chamberlain, 1991).

Study of the central projections of the "optic nerve" in vent animals and comparison of the terminal patterns with those in related surface species will provide information about similar or different uses that the animals have for their eyes. For example, imaging and light detection may well require rather different central

processing that may be reflected in the central innervation pattern. Finally, the chemical molecules used by neurons in the visual system for communication should be examined. Generally, these neurotransmitter molecules are fairly well conserved during evolution. Neuroanatomical localization of neurotransmitters in vent animals and comparison with surface forms may provide information about how extensive the evolutionary adaptation really is. Although initial studies should focus on vent shrimp, other vent taxa, especially motile species where visual orientation might be of particular advantage, should be examined for the presence of functional visual organs and visual behavior.

B.1c Physiological and Behavioral Investigations

Determining the "visual" capability of the several species of shrimp discovered around hydrothermal vents is important in understanding how their "eyes" help them function in the vent environment. In *Rimicaris exoculata*, which has the most highly modified eyes with large amounts of light-absorbing cell membrane, the light-sensitive pigment appears to be similar to the pigment responsible for night-vision in the eyes of humans: the molecule absorbs green light best, but responds to light from blue to orange in the light spectrum. We expect that the cells of the eye will report this information to the brain and determine the limits of the animal's behavior.

These expected characteristics of the eye are not well-matched to the observed available light from the vents, which is very dim and shifted towards the infrared. Two hypotheses have arisen about the function of light receptors of organisms found at the vent sites. The first suggests that these extremely modified photoreceptors may be an adaptation to aid the shrimp in identifying and avoiding lethally hot water being emitted from black smokers and for localization of optimum food resources. The light receptor of *Rimicaris exoculata* has undergone significant structural modifications in order to maximize collection of all the available light, and one would expect the visual pigment to be similarly modified for greater sensitivity at longer wavelengths. Evidence that visual pigments have been adapted for the photic environment is abundant in shallow water crustaceans. For example, eyes of mysids inhabiting a lake whose water preferentially transmits longer wavelengths (600-700 nm) contain a visual pigment whose peak absorption is at 570 nm (Lindström and Nilsson, 1988).

One possible situation which would resolve the mismatch between available light and absorption characteristics of the pigment in *Rimicaris exoculata* is that in which the eye contains another visual pigment which responds better to deep red light, but which is not present in sufficient quantity to have been observed by the biochemical methods used on *R. exoculata*. If this situation were to occur, it would be similar to that in humans: We have 3 types of pigments for sampling all parts of the visible light spectrum, and one which is used for vision at night. This is clear from human behavior and from ERG studies. But biochemical studies of the sort used on shrimp would reveal only one visual pigment for humans, the one which is preponderant numerically, i.e., the one used for night vision. Related to this is the question of whether juvenile shrimp contain the same visual pigment(s) as the adults. It is conceivable that juveniles need to respond to light of wavelengths different from adults, perhaps to find food sources different from those exploited by the adults.

The significance of the apparent mismatch between the sensitivity of the visual pigment and the available light may be understood by using a variety of techniques from electrophysiology. By measuring the electroretinogram (ERG, the voltage developed by the whole eye when light falls on it), we can determine the spectral response of the photoreceptor cells. We can investigate what the output from the eye is by using intracellular electrodes to study the response of the individual photoreceptor cells to light and possibly by examining light-evoked responses in the output fibers from the eye to the brain. Finally, the responses of cells in the brain to light delivered to the eye can be observed using extracellular electrodes.

A second hypothesis regarding the function of the photoreceptors in the vent shrimp suggests that this organism may be using its photoreceptors to locate a black smoker from some distance away (see Section 1b). Long distance vision implies detection of wavelengths that are not immediately absorbed by seawater. Visible light comprising the tail of the thermal spectrum generated by high temperature vents may be one source of transmitted light. Light generated by mats of bioluminescent microorganisms remains a plausible alternative source of transmitted visible light to which the shrimp are sensitive.

Photoreceptor cells in many species are spontaneously active in complete darkness. The level of this activity depends on the absorption characteristics of the visual pigment in the eye and on temperature, increasing with increasing temperature. From the point of view of an animal using vision under very dim light conditions, this activity constitutes noise which must be overcome. This can be done by reducing the noise in the photoreceptor cell itself, such as is done by the horseshoe crab, *Limulus polyphemus*, when its central biological clock prepares the animal's photoreceptor cells for nighttime light levels (Kaplan and Barlow, 1980). Intracellular studies of spontaneous activity in the vent shrimp will thus be particularly interesting. If the eye serves a visual function, we would expect the spontaneous activity in their photoreceptors to be extremely low, given the low intensity light near the vent sites. On the other hand, if the cells have a high level of spontaneous activity, they might serve a different function. Even if there are no sources of light, the intrinsic noise in the photoreceptor may serve as a temperature sensor through the temperature dependence of the noise. In this scenario, the cell is conceived of as reporting the temperature of the eye, and hence of the environment with which it is in equilibrium, to the brain through the intrinsic activity: The higher the level of noise, the hotter the environment. Perhaps this would be of use in helping the animals find sources of food, or to avoid the hot regions of the vents. Several considerations lead us to believe that the eye would not serve this latter function. The shrimp are viable in the temperature range 2-20°C; in other species, intrinsic photoreceptor noise would be expected to increase only by a small factor over this range. Furthermore, the temperature increases from the ambient temperature of seawater (2°C) to the maximum temperature at the core of the vent water (> 350°C) over a distance of less than 3 cm. The shrimp are rapid swimmers and thus the temperature of the eye can be expected to lag behind that of the water around the eye. This might prove fatal near the narrow transition zone around the vent jet, if this were the principal mechanism used by the shrimp to avoid the hot water of the jet.

When we know the response of the eyes to light throughout the spectrum of light from 400 to 1000 nm, we will have a better idea of what light cues the shrimp can respond to. The questions then become: Are there sources of light matching the visual sensitivity of the shrimp? Are there other sources of light, such as luminescence of biological or chemical origin, which might match more closely the light-absorbing characteristics of the pigment molecule studied so far in *Rimicaris exoculata*? How do the various species of shrimp use the light information available? Are they sufficiently visually sensitive to use near-infrared light to orient on the vents or visible light to locate new vents from afar? Experiments designed to discover and study visually-guided behavior become possible once the visual capabilities of the animals are known

There has been some concern expressed about the lack of a startle response by the shrimp in response to the extremely bright lights of the submersible. However, this is not entirely unexpected if the shrimp actively searches for light, whether attempting to locate a black smoker site or to find food. Coming from an environment where the shrimp never experiences high light levels, one would not expect high light levels to be correlated with a startle response. Similar observations have been made from submersibles on deep-sea, non-migrating fish. They also are not bothered by the sudden bright lights of the submersible, but continue with their "normal" swimming patterns. Observations under conditions which avoid high light levels are highly desirable to determine whether behavior of the vent community is severely altered by the presence of lights of submersibles.

Most of the structural and physiological research must be performed in the laboratory, in an environment vastly different from that in which the shrimp live. The methods developed to study the visual capabilities

of the shrimp may be adaptable to determining the visual capabilities of other vent fauna, both vertebrate (e.g., the fish observed near some of the vents) and invertebrate (e.g., the crabs found in some of the vent communities). The existence of vision in members of a vent community raises questions not only about the use of vision to find or avoid the vents or to locate food, but also about its use in interactions between members of the community.

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APPENDIX I

CALCULATION OF OBSERVED PHOTON FLUX AND PREDICTED BLACKBODY FLUX

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Observed Photon Flux

CCD camera images taken on *Alvin* dives may be used to calculate the photon flux a specific distance from the source. A given CCD image of the scene contains information on the scene brightness as a function of distance from the vent. We want to convert this to the photon flux some distance from the vent due to all sources of light at the vent. There are two methods of proceeding, with some steps in common. One method would be to place a calibrated light source near the vent and measure the CCD camera response through various filters. [This calibration was not actually done during the dive, so we cannot use this method]. The second method is to use the calibrations of the known response of each separate part of the CCD camera/lens system, and then invert to find the apparent luminosity per unit area (surface brightness) of the source. Then in both methods we sum over all parts of the source to get the illumination (photon flux) at some distance from these sources of light. Finally, with the known optical transmission of seawater we can express the photon flux as a function of distance from the vent.

The basic data collected are analog-to-digital units (ADU) per second at various picture elements (pixels) in the CCD scene, for a given lens, camera system, optical color filter, and distance from the vent. The flux of photons as a function of distance from the vent may be calculated from the observed data in the following way.

The gain of the CCD camera analog electronics is ADU per electron (ADU/e). The value of the inverse of this gain parameter was obtained from Marquest Group, Inc. (packagers of the camera system), Photometrics (developers ofthe camera system), and from the plot of ADU dispersion vs illumination level. All three methods agree, within error, with the value given by Marquest: 15.5 e/ADU. This is the number of electrons pixel^{-1} read^{-1} to trigger one bit in the digital image. We use this to convert from ADU sec^{-1} to electrons sec^{-1}. For some given pixel, we want to know how many photons sec^{-1} in that area of the scene were detected. To get from electron sec^{-1} to photons sec^{-1}, we must divide out the camera throughput (electrons per incident photon) at each wavelength. The two contributors to this throughput are the optical transmission of the camera optics (window, lens, and filter [if any]) and the CCD quantum efficiency (QE). Not every incident photon is converted into an electron-hole pair in the silicon. At short wavelengths the QE is low because UV and blue photons have a short mean free path, and are often absorbed in the poly-silicon gate structure before they get to the charge collection region. At long wavelengths, the red and IR photons have such a large mean free path that they often are not absorbed until they have travelled through the charge collection region. Beyond 1100 nm silicon is transparent. We use the tabulated QE as a function of wavelength of the Thomson CCD which was used in that camera. It rises from 20% at 400 nm, through a peak of 37% at 650 nm, falling to 20% at 850 nm, and trailing off to zero at 1100 nm. The camera optics (less external color filter) has 60% transmission at 400 nm, rising to 80% at 600 nm, and saturating at 85% at longer wavelengths. At each 50 nm interval, the product $T_{(optics)}$ * QE was tabulated. In the two broad wavelength bands used in the *Alvin* observations (400-750 nm and 750-850 nm), the average of this product was obtained. [850 nm is used as the long wavelength limit due to the catastrophic increase in seawater absorption at longer wavelengths]. These average throughputs are: 0.23 e/photon (400-750 nm) and 0.22 e/photon (750-850 nm), to about 5% accuracy.

The observed ADU sec^{-1} for the brightest groups of pixels in the vent scene are reported from the *Alvin* data. Using these reported scene brightness levels, we find the following values for the brightest parts of the vent scene: 80 photons $pixel^{-1}$ sec^{-1} (750-850 nm), and approximately 8.6 photons $pixel^{-1}$ sec^{-1} (400-750 nm). Both of these numbers probably are no more than 10-20% accurate, due to the nature of the time-sequenced filter observations. We must now express this as apparent luminosity (different than the true luminosity due to seawater absorption) at the vent per unit area, and then sum over vent areas of equal brightness. The camera had a f/3.5 lens, with an effective f/number of 4 immersed in seawater. Most of the data were taken at a distance of 45 cm. Thus, a 23 μm^2 pixel on the CCD subtends 0.065 cm at the vent, or an area of 0.0042 cm^2. Light from each 0.0042 cm^2 luminous patch is captured by the 4 mm (0.16 cm^2) camera lens aperture, at a distance of 45 cm. The narrowest vents are about 10 cm in diameter, so is is reasonable to say that much of the light actually comes from 5 cm inside the jet, implying a mean camera-source distance of 50 cm for these series of observations. Thus, the observed flux of photons F at this distance of 50 cm is given by the equation:

$$F_{(50cm)} = N_p * (A/.0042) / 0.16 \quad \text{photons } cm^{-2} sec^{-1}$$

where N_p = photons $pixel^{-1}$ sec^{-1}, and A = sum of areas in the vent of average brightness above the threshold in cm^2. Using the image of the vent light and the image scale (cm $pixel^{-1}$), this sum area was found to be approximately 9.3 cm^2, to about 20% accuracy. Thus,

$$F_{(50cm)} = 1.4 * 10^4 * N_p \quad \text{photons } cm^{-2} sec^{-1}.$$

Seawater absorption data may then be used to express this photon flux as a function of distance and wavelength:

$$F_{(\lambda)} = 1.4 * 10^4 * N_{p(\lambda)} * (50/D)^2 * \exp[K_{a(\lambda)}*(50-D)],$$

where D is the distance from the vent in cm.

Plugging in the above values for the observed number of photons $pixel^{-1}$ sec^{-1} incident on the CCD averaged over the two bands, N_p, and using the tabulated absorption coefficient K_a as a function of wavelength and averaging over the wavelengths within each band, we can finally write expressions for this photon flux in the two wavelength bands:

$$F_{(400\text{-}750nm)} = 1.2 * 10^5 * (50/D)^2 * \exp[0.005 * (50-D)] \quad \text{photons } cm^{-2} sec^{-1}$$

$$F_{(750\text{-}850nm)} = 1.1 * 10^6 * (50/D)^2 * \exp[0.024 * (50-D)] \quad \text{photons } cm^{-2} sec^{-1},$$

where the 1-sigma statistical plus systematic errors are about 30% for the 750-850 nm band and as high as 50-100% for the 400-750 nm band.

It is interesting to extrapolate to an observed red photon flux at a distance of 5 cm:

$$F_{(5cm,\ 750\text{-}850nm)} = 3.2 * 10^8 \quad \text{photons } cm^{-2} sec^{-1}.$$

While the observed vent light appears to be quite red, it is premature to conclude that all of the vent light is due to blackbody emission from the hot vent water, particularly since the green light flux is poorly known and also because the thermal photon emissivity of the vent water is unknown.

Estimated Hot Vent Blackbody Photon Flux

Is is possible that this observed flux can be due to the thermal light from the hot vent water? It is useful to estimate the flux of photons expected from a 350°C blaekbody, for some assumed emissivity. Below is a heuristic derivation of the blackbody radiation which may be useful in our case. An exact derivation may be found in several references: Planck, M., The Theory of Heat Radiation, 1913, repro. Dover (NY, 1959); Tolman, R. C., The Principles of Statistical Mechanics, Oxford U. Press (1962); Eisberg, R. and Resnick, R., Quantum Physics, 2nd Edition, Wiley (1985). An exhaustive discussion may be found in: Siegel, R. and Howell, J., Thermal Radiation Heat Transfer, (McGraw-Hill, 1972).

Any medium which is capable of absorbing light is capable of emitting thermal photons. Each scattering of a photon results in a transfer of energy, sometimes to and sometimes from the thermal bath. In thermal equilibrium, a medium which scatters photons many times before it can escape will reach an equilibrium spectrum of thermal photons given by the equipartition between the thermal energy available for scattering and the mean photon energy. The ratio of photon energy to thermal energy is

$$x = h \upsilon / k T = 1.439 \times 10^{4} / (\lambda_0 T)$$

where h is Planck's constant, υ is the frequency in Hz, k is the Boltzman constant, λ_0 is the vacuum wavelength in μm, and T is the absolute temperature in deg Kelvin. Note that this ratio of energies, which enters the probability of thermally exciting a photon of frequency υ (below), depends only on the photon frequency (or wavelength in vacuum) -- not the wavelength of the photon in the medium -- and the temperature. For a perfectly absorbing medium (blackbody) at 350°C (623°K), $x = 23.1 / \lambda_0$, where λ_0 is expressed in μm.

The oscillators in a thermal bath may be treated as normal modes of a cavity. We want the number of independent modes of electromagnetic waves per unit volume. For an emissivity of 1, every cc of the medium will contain the maximum number of blackbody thermal photons given by the product of the number of independent modes, proportional to $(2 \text{ cm}/\lambda)^3$, and the Bose-Einstein probability that a mode of energy hν is excited, 1/[exp(x) - 1]. Each side of the 1 cm cube (except for the side bordering the cold water) has as many thermal photons entering per second as leaving. The number leaving each side, including the outer side, is then given by the product of the number of photons inside the cube times the rate at which a photon of wavelength λ crosses the face, c/λ, where c is the velocity of light in vacuum. Here λ is the photon wavelength in cm, in the water (proportional to the refractive index n).

For simplicity, the above derivation has wavelengths in cm. The exact expression for the photon emittance per square cm per second per unit wavelength (cm) radiated into 2π steradians is:

$$N_{(\lambda 0)} = 2\pi c \ n^2 / \{\lambda_0^4 \ [\exp(x) - 1]\}.$$

Converting to microns, the resulting surface brightness, or emittance, of thermal photons per micron wavelength interval is:

$$N(\lambda_0) = 1.88 \times 10^{23} \ n^2 / \{\lambda_0^4 \ [\exp(x) - 1]\} \quad \text{cm}^{-2} \ \text{sec}^{-1} \ \mu\text{m}^{-1},$$

where the vacuum wavelength λ_0 is in μm, x is the ratio of photon energy to effective thermal energy (given above), and n is the refractive index of the medium at the wavelength of observation.

Each cm^2 of a blackbody at temperature T radiates this number of thermal photons into 2π steradians solid angle. The total radiant thermal photon luminosity is then obtained by integrating the above relationship over the surface of the blackbody emitter. For a temperature of 650K, and assuming unit emissivity, $x = 23.1/\lambda_0$ (units for λ_0 are μm). Using a refractive index for seawater of 1.3, we obtain for example an

emittance of 2.3 x 10^{11} photons cm^{-2} sec^{-1} in a 100 nm band cemtered at 800 nm, for every square cm which is at this temperature, assuming an emissivity of 1. Kirchoff's law gives a relation between the reflectivity and emissivity of a greybody. The emissivity of vent seawater is almost certainly less than 1, unless it is at the critical point (critical opalescence). For an emissivity of 0.3, the photon emittance in the above example is reduced by a factor of 3 to 7.7 x 10^{10} photons cm^{-2} sec^{-1} radiated into one hemisphere. How does this compare with the observed flux 50 cm away?

As in the previous section, to convert to flux at some distance we must sum over all parts of the source with this surface brightness, then attenuate the flux by the known seawater attenuation (0.30 at 800 nm and 50 cm distance), and then divide by the area of a half-sphere of radius 50 cm to get the flux through a 1 cm^2 patch. The predicted thermal photon flux in the wavelength band 750-850 nm 50 cm from a greybody emitter of emissivity 0.3, temperature 650°K, and area of 9.3 cm^2 is then 0.30 x 7.7 x 10^{10} / 1.6 x 10^4 = 1.4 x 10^6 photons cm^{-2} sec^{-1}. This is roughly equal to the observed flux in this band; an emissivity of 0.25 would give exact agreement with the observation. It will be important to measure the reflectivity and/or transmission of the vent water as a function of wavelength.

APPENDIX II

SONOLUMINESCENCE AND THE DIFFUSE LIGHT EMISSION FROM HYDROTHERMAL VENTS

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Abstract

Caviation, the implosion of a bubble in a liquid, creates microregimes in which temperatures in excess of 5000° may be attained. Sonochemical processes associated with caviation events in water generate reactive species such as hydroxyl radical, hydrated electrons and hydrogen peroxide. The sonoluminescence spectrum of seawater is characterized by emission at 589 nm due to excited-state sodium. Excited-state Na atoms are produced from the reaction of Na^+ with high-energy hydroxyl radicals formed directly during the cavitation event. Although other dissolved cations are present in seawater, their characteristic emission lines are not observed because of their low concentrations relative to sodium. Hydrothermal vent water should have a sonoluminescence spectrum nearly identical to seawater, although the effect which dissolved hydrogen sulfide has is unknown. Unless elemental sulfur is produced during caviation in vent waters, it is unlikely that sonoluminescence can account for the diffuse light emission observed in hydrothermal vent discharges.

BACKGROUND SUMMARY

Cavitation and sonochemical processes have been suggested as widespread natural phenomena that occur in the oceans, especially during the breaking of waves (Anbar, 1968). The compression of gas bubbles during cavitation gives rise to intense localized heating generating temperatures of ~ 5000 K (Flint and Suslick, 1991a). Sonolysis of water leads to the formation of highly reactive species such as hydrogen peroxide, hydroxyl radical, and hydrated electrons (Suslick, 1990), components which are generally associated with photochemical processes in the oceans (Zika, 1987).

The experiments carried out by Anbar (1968) over twenty years ago used a teflon-lined rotary pump to focus a jet stream of 0.8 M NaCl onto a water surface. Light emission at 589 nm, apparently resulting from the excitation of sodium atoms, was used as a criterion for cavitation in the region of impact. Anbar inferred that cavitation takes place when water impinges on water at relatively low linear velocities. Although acoustic techniques and *in situ* 3-D holographic imaging have been used to successfully observe cavitation nuclei produced during the breaking of waves, the formation of whitecaps and from biological activity (O'Hern, 1987), whether the cavitational collapse of bubbles and sonolysis take place in the oceans is unknown. The actual temperatures and pressures created as the result of the collapse of the bubbles associated with these oceanic processes have yet to be determined.

Ultrasound provides a means for creating acoustic cavitation in the laboratory (Suslick, 1990). During the violent collapse of the bubbles produced by ultrasound, the incapsuled gases and solvent vapor are rapidly heated causing them to react. Sonoluminescence associated with acoustic cavitation provides a spectroscopic probe of the species and conditions produced during cavitation (Flint & Suslick, 1989, 1991a, 1991b). The emission from sonoluminescence in aqueous solutions is extremely fast and is estimated to occur on time-scales of < 100 ps (Barber & Putterman, 1991).

We have recently used ultrasound to create acoustic cavitation in seawater, and measured the resulting sonoluminescence (Becker et al. 1992). The sonoluminescence spectra of seawater (a), the sodium chloride control (b) and tapwater (c) are shown in Figure 1. The spectrum for both the seawater sample and the sodium chloride control show a single emission feature at around 589 nm with similar intensity and band width. The emission at 589 nm has been observed previously in the sonoluminescence spectrum of sodium salts in water (Anbar, 1968; Taylor and Jarman, 1970; Sehgal et al., 1979; Flint and Suslick, 1991b) and corresponds to the emission line of excited-state sodium. Although seawater contains other alkali-metal ions, their concentrations are much less than sodium, and thus the intensity of emission lines associated with the excited states of these ions is too weak to be observed.

From the Flint and Suslick (1991b) alkali metal ion sonoluminescence studies, the following reactions can be used to explain the seawater observations:

$$H_2O \overset{)))}{\longrightarrow} H\cdot + HO\cdot \qquad (1)$$

$$H\cdot + Na^+ \longrightarrow Na + H^+ \qquad (2)$$

$$H\cdot + OH\cdot + Na \longrightarrow Na^* + H_2O \qquad (3)$$

$$H\cdot + NaOH \longrightarrow Na^* + H_2O \qquad (4)$$

$$Na^* \longrightarrow Na + h\nu \qquad (5)$$

$$Na^* + S \longrightarrow Na + S + \text{heat} \qquad (6)$$

The symbol $\overset{)))}{\longrightarrow}$ denotes ultrasonic induced cavitation. Radicals produced from the ultrasonic irradiation of water are shown in eq. 1. The radicals H· and OH· are formed in the hot spot of the cavitation event. High energy radicals produced from solvent vapor in the cavitation event diffuse out of the hotspot where they react to produce excited state atoms. These H· and OH· radicals are capable of both reducing Na+ to atoms and promoting atoms to the excited state via chemiluminescence (eqs. 2 and 3). The reaction in eq. 2 was proposed by Taylor and Jarman (1970) for the sonoluminescence from NaCl solutions. A third possibility is that the cation is excited and reduced in one step (eq. 4)

(Riesz, Kondo and Krisna, 1990). The excited atom can either emit a photon (eq. 5) or can be totally quenched by a solvent molecule (eq. 6). The rapid quenching by solvent leads to resonance line broadening in the sonoluminescence spectra of seawater and of NaCl and other alkali-metal ion solutions.

These reactions explain the sonoluminescence from nonvolatile species such as Na^+ ion which would not be expected to be present inside the cavitating bubble. The effective concentration of the solvent in the secondary reaction zone, and thus the rate of quenching and the lifetime of the excited state, is essentially independent of the solvent, solvent vapor pressure, or gas thermal conductivity.

DIFFUSE LIGHT EMISSION ASSOCIATED WITH HYDROTHERMAL VENT DISCHARGES

The processes responsible for the diffuse light emission observed in deep ocean hydrothermal vent discharges (Van Dover, 1988/89; Van Dover et al., 1988) are not known. The report (Van Dover et al., 1988) that the light is not detectable by the non light-adjusted human eye indicates that the emission wavelength is >750 nm. This has apparently been confirmed by observations of the light using various cut-off filters (Van Dover, personal communication). It does not appear the hydrothermal diffuse light emission can be accounted for by the sonochemical formation of excited-state sodium, or the excited-states of other vent metal ions, produced from collapsing bubbles which may be present in vent waters. In Table I, we have estimated the wavelengths and intensities (relative to sodium) of the main emission lines characteristic of seawater and hydrothermal vent water. Although potassium emits in the region of spectrum where hydrothermal vent water emission is observed, potassium emission should be much less intense than that of sodium. Since no emission is apparently observed at 589 nm, it is unlikely that the vent emission is from excited-state alkali-metal ions. However, the effect of H_2S in vent waters on sonoluminescence, and its sonochemical reactions during caviation, are unknown. The

formation of excited-state elemental sulfur could result in emission at 920 nm; a possible caviational induced reaction sequence is the following:

$$H_2S + OH\cdot \text{ -------> multisteps ------> } SO_2$$

$$2H_2S + SO_2 \text{ -------> } 3S + 2H_2O$$

$$H\cdot + OH\cdot + S \text{ ---------> } S^* + H_2O$$

$$S^* \text{ ---------> } S + h\nu$$

However, it is difficult to imagine the formation of excited-state sulfur occurring without the simultaneous formation of excited-state sodium and its characteristic 589 nm emission. It is possible that intermediates associated with caviational reactions involving H_2S quench excited-state sodium and thus prevent 589 nm emission. Further investiagtions of the sonoluminescene spectra of alkali-metal ion solutions containing H_2S are required to evaluate this possibly.

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TABLE I: ESTIMATED SONOLUMINESCENCE INTENSITIES+ (RELATIVE TO SODIUM) FOR SEAWATER AND HYDROTHERMAL VENT WATER

	emission (nm)	seawater concentration	seawater sonoluminescence	vent water concentration	vent water sonoluminescence
Na+	590	1.0*	1.0++	1.0**	1.0++
K+	770 (doublet)	0.02	0.07	0.04	0.14
Li+	670	$5x10^{-5}$	$1.7x10^{-5}$	$8x10^{-4}$	$3x10^{-4}$
S	920	0.028 ($SO_4^=$)	??	0.01 (H_2S)	??

+ Based on results in Flint and Suslick, 1991b and Becker et al., 1992.

* $[Na^+] = 0.468$ mol l^{-1}

++ The sonoluminescence intensity of the sodium emission is assumed to be roughly the same in both seawater and hydrothermal vent water, and have a value of 375 (arbritary units).

** $[Na^+] = 0.5$ mol kg^{-1}

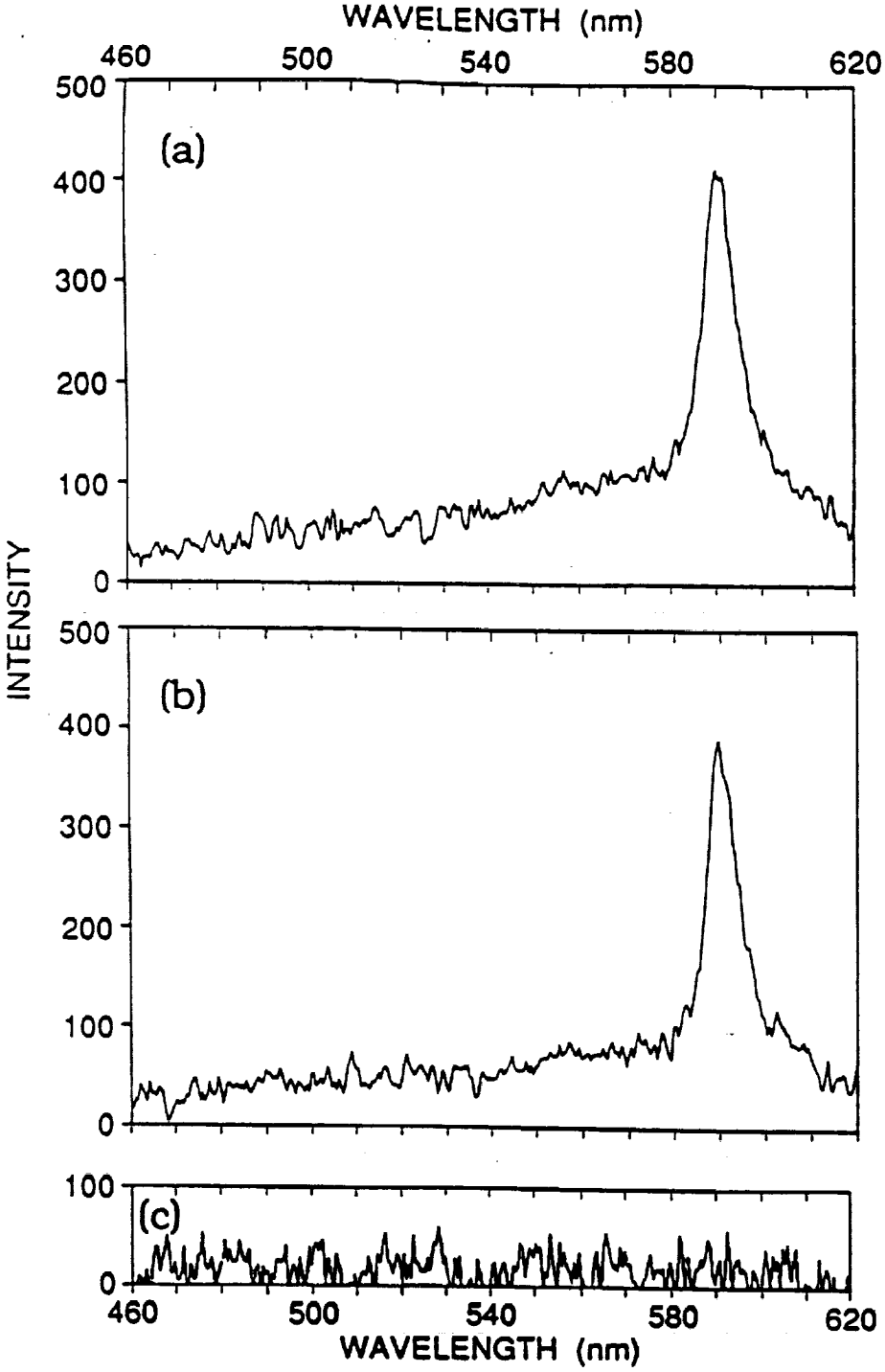

Fig. 1. Sonoluminescence spectra of (a) deep water from the North Atlantic, (b) 10.65 g l^{-1} NaCl control and (c) tap-water. The spectral measurements were carried to longer wavelengths, but no emission features were observed. There are no distinguishable differences between seawater samples of surface and deep-oceanic waters.

APPENDIX III.

Is the Light Emitted from Black Smokers a Chemiluminescence?

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On a cruise (RV Oceanus, ~ August 1983), during which I was taking samples and examining for the presence bioluminescent bacteria, I also had the occasion to measure the light emission in the visible range from core samples taken at the Grand Banks, off St. Johns, NFL. Measurements were made on muds from the bottom to ~50 cm beneath the surface. Light emission was determined by photon counting in a shipboard Beckman liquid scintillation counter at room temperature with the coincidence circuit turned off so as to detect single photons rather than bursts of photons, as in counting radioactivity.

Mud samples were removed from the core with a spatula and placed in scintillation vials without treatment or additions. Signals were high and continued on a time scale of hours, but with evident decay in count rates. By removing the vial and stirring the contents with the spatula a higher count rate was restored. The possibility that this was due to the exposure to room light (e.g., phosphorescence) was checked and rejected. It was concluded at the time that this could be attributed to the chemiluminescence of reduced organic compounds by direct reaction with molecular oxygen. Anaerobic mud samples from a similar but shallow locations (e.g., Eel Pond) should be checked for light emission in a similar way.

The oxidation of many reduced organic compounds is known to result in a low quantum yield light emission. In a few cases the approximate spectral distributions have been estimated and reported to peak in the 500 nm range. Because of the low yield it has been impossible to ascertain intermediates and products, but in reactions with higher yields peroxides are known intermediates with excited carbonyls being produced.

I believe that the light emission reported from black smoker plumes from deep sea hydrothermal vents could be due to a chemiluminescence of this type. The vent material includes reduced organic material, and is being mixed with oxygen in the plumes. The high temperatures would result in rapid reaction rates, so emission intensities could be substantial. The reported wavelengths of such chemiluminescence are in the range of the absorption peaks of putative photoreceptor pigments found in animals living near the vents.

As suggested by my colleague, Dr. Thérèse Wilson, the distinction between chemiluminescence and thermal (black body) radiation can be made by determining whether or not the vent emission is enhanced by a fluorescent probe. Chemiluminescent reactions of the type suggested generally occur via radical mechanism result in the production of an array of excited states, typically triplets, that are themselves poor emitters. Molecules such as dibromoanthracene have been shown to intercept such exited states and to produce singlets that do emit, increasing the emission by many fold. Black body radiation should be altogether unaffected b probes of this type. Could such probes be injected into vent water where emission is occurring and the enhancement (or not) of the light emission recorded by a CCD camera? (In the report, no mention is made of the exposure time for an individual frame.

APPENDIX IV.

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